Tandem Olefin Metathesis/Oxidative Cyclization: Synthesis of Tetrahydrofuran Diols from Simple Olefins

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Supporting Information

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1. General Information

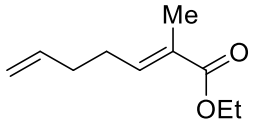
Solvents were purified by passage through solvent purification columns and further degassed with argon.[1] Commercially available liquid reagents were degassed by three freeze pump thaw cycles (for volatile substrates) or under vacuum (for nonvolatile substrates) prior to entering the glove box. Terminal olefins, sodium periodate and $CeCl_3$ heptahydrate were purchased from Aldrich and used as is.

Standard NMR spectroscopy experiments were conducted on a Varian INOVA 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz) or a Bruker Avance HD 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, equipped with a cryoprobe) spectrometer. Chemical shifts are referenced to the residual solvent peak (TMS). Multiplicity is reported as follows: (s: singlet, d: doublet, t: triplet: q: quartet, br: broad, m: multiplet). Spectra were analyzed and processed using MestReNova. High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using JEOL JMS-600H High Resolution Mass Spectrometer.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* **1996**, *15*, 1518-1520.

2. Experimental

i) Synthesis of substrates

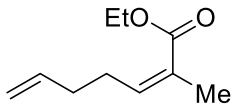


ethyl (E)-2-methylhepta-2,6-dienoate (5a): Synthesized according to the general procedure from Murphy *et al*.[2] An oven-dried round bottom flask was flushed with argon and triethyl 2-phosphono propionate (2.30 mL, 11.0 mmol, 1.1 equiv) was added to a stirring solution of NaH (60% dispersion in mineral oil, 0.440 g, 11 mmol, 1.1 equiv) in anhydrous THF (30 mL) at 0 °C. After 30 minutes, 4-pentenal (0.987 mL, 10.0 mmol, 1.0 equiv) was then added dropwise and the reaction was stirred for 30 minutes at 0 °C. The reaction was allowed to warm to ambient temperature and stirred for an additional 3 hr. The reaction mixture was quenched with water (20 mL) and diluted with EtOAc (60 mL). The separated organic phase was then washed with brine (20 mL), dried with Na_2SO_4 and concentrated *in vacuo* to yield a crude 5.9:1 mixture (E:Z). R_f (5% Et_2O in hexanes): 0.55 (Z isomer), 0.45 (E isomer). The title compound was purified by silica gel column chromatography (1% to 1.5% Et_2O in hexanes) to yield a clear colorless oil (1.056 g, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.74 (tq, *J* = 7.3, 1.5 Hz, 1H), 5.81 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.00 (ddt, *J* = 10.2, 1.9, 1.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.30- 2.17 (m, 4H), 1.84 (dd, *J* = 1.6, 0.8 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 168.6, 141.7, 128.6, 115.7,

[2] Murphy, S. K.; Coulter, M. M.; Dong, V. M. *Chem. Sci.* **2012**, *3*, 355–358.

60.9, 33.0, 28.5, 14.7, 12.8. HRMS (EI$^+$): *m/z* calculated for $[C_{10}H_{16}O_2]^+$: 168.1150, found: 168.1146.

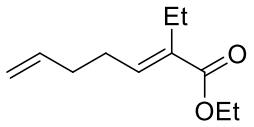
Note: The Z isomer was also isolated (66 mg, 4%). For a more selective synthesis of the Z isomer, see the following Still-modified HWE procedure.



ethyl (Z)-2-methylhepta-2,6-dienoate (5b): Synthesized according to the Still-modified HWE procedure reported by Snider and Kiselgof.[3] An oven-dried round bottom flask was flushed with argon and charged with 18-crown-6 (13.2 g, 50.0 mmol, 5.0 equiv). THF (200 mL) and triethyl 2-phosphono propionate (2.14 mL, 10.0 mmol, 1.0 equiv) were added, and the flask was cooled to -78 °C. KHMDS (20 mL, 0.5 M in Toluene, 10.0 mmol, 1.0 equiv) was then added dropwise, with the solution turning pale orange towards the end of the addition. 4-pentenal (0.987 mL, 10.0 mmol, 1.0 equiv) was then added, and the mixture was stirred at -78 °C for 90 minutes. The reaction was warmed to -30 °C, and then quenched with saturated NH_4Cl (30 mL). The mixture was extracted with Et_2O (2 x 75 mL) and the combined organic phases were washed with brine (50 mL), dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was determined to be a 1:2.5 mixture (E:Z). The title Z isomer was isolated by column chromatography (1% to 2.5% Et_2O in hexanes) to yield a clear colorless oil (397 mg, 24%). ^{1}H NMR (400

[3] Snider, B. B.; Kiselgof, J. Y. *Tetrahedron* **1998**, *54*, 10641–10648.

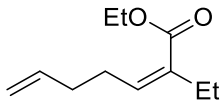
MHz, $CDCl_3$, ppm) δ 5.92 (tq, *J* = 7.3, 1.5 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.97 (ddt, *J* = 10.2, 2.0, 1.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.55 (qq, *J* = 7.4, 1.4 Hz, 2H), 2.16 (dtt, *J* = 7.3, 6.6, 1.3 Hz, 2H), 1.89 (q, *J* = 1.4 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 168.5, 142.4, 138.4, 128.0, 115.4, 60.5, 33.8, 29.2, 21.0, 14.7. HRMS (EI^+): *m/z* calculated for $[C_{10}H_{16}O_2]^+$: 168.1150, found: 168.1146.



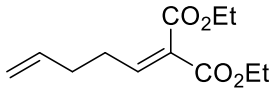
ethyl (E)-2-ethylhepta-2,6-dienoate (5c): An oven-dried round bottom flask was flushed with argon and triethyl 2-phosphonobutyrate (2.61 mL, 11.0 mmol, 1.1 equiv) was added to a stirring solution of NaH (60% dispersion in mineral oil, 0.440 g, 11 mmol, 1.1 equiv) in anhydrous THF (30 mL) at 0 °C. After 30 minutes, 4-pentenal (0.987 mL, 10.0 mmol, 1.0 equiv) was then added dropwise and the reaction was stirred for 30 minutes at 0 °C. The reaction was allowed to warm to ambient temperature and stirred for an additional 3 hr. The reaction mixture was quenched with water (20 mL) and diluted with EtOAc (60 mL). The separated organic phase was then washed with brine (20 mL), dried with Na_2SO_4 and concentrated *in vacuo* to yield a crude 5.9:1 mixture (E:Z). R_f (5% Et_2O in hexanes): 0.55 (Z isomer), 0.45 (E isomer). The title compound was purified by silica gel column chromatography (1% to 1.5% Et_2O in hexanes) to yield a clear colorless oil (398 mg, 22% yield). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 6.70 (t, *J* = 7.3 Hz, 1H), 5.82 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.6 Hz, 1H),

5.00 (d, *J* = 10.2 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.35 – 2.24 (m, 4H), 2.23 – 2.15 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 168.0, 141.0, 137.7, 134.6, 115.4, 60.5, 33.0, 27.9, 20.2, 14.4, 14.0; HRMS (EI$^+$): *m/z* calculated for $[C_{11}H_{19}O_2]^+$: 183.1385, found: 183.1401.

The Z-isomer was also isolated from this reaction:



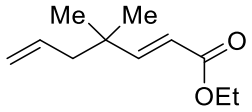
ethyl (Z)-2-ethylhepta-2,6-dienoate (5d): The Z-isomer was isolated from the early fractions of the column to yield a clear oil (147 mg, 8% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 5.87 – 5.76 (m, 2H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.98 (ddt, *J* = 10.2, 2.0, 1.2 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.51 (q, *J* = 7.6 Hz, 2H), 2.27 (qq, *J* = 7.4, 1.2 Hz, 2H), 2.17 (q, *J* = 7.4 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 139.3, 138.0, 134.2, 115.0, 60.1, 33.5, 28.7, 27.5, 14.3, 13.7. HRMS (EI$^+$): *m/z* calculated for $[C_{11}H_{19}O_2]^+$: 183.1385, found: 183.1410.



diethyl 2-(pent-4-en-1-ylidene)malonate (5e):

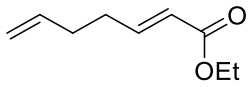
To a solution of 4-pentenal (0.987 mL, 10 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added diethyl malonate (1.68 mL, 11 mmol, 1.1 equiv), glacial acetic acid (57 µL, 1 mmol, 0.1 equiv) and piperidine (99 µL, 1 mmol, 0.1 equiv). The mixture was stirred at room temperature for 6.5 hr, at which point it was diluted with 100 mL EtOAc, washed with $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4 and

concentrated *in vacuo*. The title compound was purified by column chromatography (5-10% EtOAc in hexanes) to yield a clear and colorless oil (314.3 mg, 14%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.99 (t, *J* = 7.7 Hz, 1H), 5.80 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.10-5.00 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.41 (q, *J* = 7.5, 7.1 Hz, 2H), 2.28-2.21 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 163.9, 148.5, 136.7, 129.0, 115.9, 61.3, 61.2, 32.2, 29.0, 14.2, 14.1; HRMS (EI+): *m/z* calculated for $[C_{12}H_9O_4]^+$: 227.1283, found: 227.1291. Note: the main byproduct was assigned as the aldehyde homoaldol/dehydration product (577 mg, 77%).



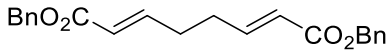
ethyl (*E*)-4,4-dimethylhepta-2,6-dienoate (5f): An oven-dried round bottom flask was flushed with argon and charged with NaH (0.359 g, 9.0 mmol, 1.5 equiv) and THF (20 mL). The stirring mixture was cooled to 0 °C, and triethylphosphonoacetate (1.789 mL, 9.0 mmol, 1.5 equiv) was added. After 20 minutes, 2,2-Dimethyl-4-pentenal (0.815 mL, 6.0 mmol, 1.0 equiv) was then added dropwise and the reaction was stirred for 30 minutes at 0 °C. The reaction mixture was allowed to warm to ambient temperature and refluxed at 80°C for 2 hours. The reaction mixture was quenched sequentially with a saturated Na_2CO_3 solution (5 mL), water (5 mL), and brine (5 mL). Diethyl ether (5 mL) was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 x 5 mL). The combined organic phases were dried over Na_2SO_4 and

concentrated *in vacuo*. The title compound was purified by silica gel column chromatography (2% EtOAc in Hexanes) to give a clear colorless oil (1.19 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$,ppm) δ 6.93 (d, *J* = 15.9 Hz, 1H), 5.72 (d, *J* = 15.9 Hz, 1H), 5.70 (ddt, *J* = 16.8, 10.2, 7.4 Hz, 1H), 5.06 – 4.99 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.11 (dt, *J* = 7.3, 1.2 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 157.8, 134.4, 118.1, 117.9, 60.4, 46.5, 36.9, 26.3, 14.4. HRMS (EI+): *m/z* calculated for $[C_9H_{14}O_2]^+$: 154.0994, found: 154.0990.



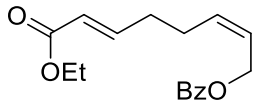
ethyl (E)-hepta-2,6-dienoate (5g): An oven-dried round bottom flask was flushed with argon and triethylphosphonoacetate (1.789 mL, 9.0 mmol, 1.5 equiv) was added to a stirring solution of NaH (60% dispersion in mineral oil, 0.359 g, 9.0 mmol, 1.5 equiv) in anhydrous THF (20 mL) at 0 °C. After 20 minutes, 4-pentenal (0.592 mL, 6.0 mmol, 1.0 equiv) was then added dropwise and the reaction was stirred for 30 minutes at 0 °C. The reaction was allowed to warm to ambient temperature and stirred for an additional 2 hours. The reaction mixture was quenched sequentially with a saturated Na_2CO_3 solution (5 mL), water (5 mL), and brine (5 mL). Diethyl ether (5 mL) was added and the organic layer was separated. The aqueous layer was extracted with 3 x 5 mL ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo*. The title compound was purified by silica gel column chromatography (2% EtOAc in Hexanes) to give a clear colorless oil (0.814 g, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.95 (dt, *J* = 15.6, 6.7 Hz, 1H), 5.79-8.84 (m, 2H), 5.05(dq, *J* = 17.1,

1.6 Hz, 1H), 5.00 (ddt, *J* = 10.2, 1.8, 1.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.33 – 2.27 (m, 2H), 2.25 – 2.19 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 166.8, 148.4, 137.2, 121.8, 115.7, 60.3, 32.2, 31.6, 14.4. HRMS (EI^+): *m/z* calculated for $[C_9H_{14}O_2]^+$: 154.0994, found: 154.0990.



dibenzyl (2E,6E)-octa-2,6-dienedioate (1): A 100 mL 2-neck round bottom flask was charged with **Ru-2** (G2, 84.9 mg, 0.1 mmol, 0.025 eq) and equipped with a Teflon-coated stir bar and a water-cooled reflux condenser. The flask and condenser were evacuated and refilled with Ar twice. CH_2Cl_2 (20 mL) was then added, followed by 1,5-cyclooctadiene (491 µL, 4.0 mmol, 1 eq) and benzyl acrylate (2.94 mL, 19.2 mmol, 4.8 eq). The resulting mixture was heated to reflux under a flow of Ar for 4 hr, and then cooled to ambient temperature. The crude mixture was diluted with EtOAc (100 mL) and washed with brine (20 mL). The organic extract was dried with Na_2SO_4 and concentrated *in vacuo*. The title compound was isolated by column chromatography (10-15% EtOAc in Hexanes) to give a yellow oil (1.723 g). A sample of this material was used in an oxidative cyclization control experiment (see General Procedure A, without Ru catalyst), and 7% conversion was observed. This result indicates that the isolated dienoate after column chromatography likely still contains trace residual Ru. To further remove trace Ru, the dienoate was dissolved in Et_2O (10 mL) and 1.0 g of Siliabond DMT (purchased from Silicycle) was added. The suspension was stirred at ambient temperature for 2 hr, whereby the organic phase became a lighter yellow. The

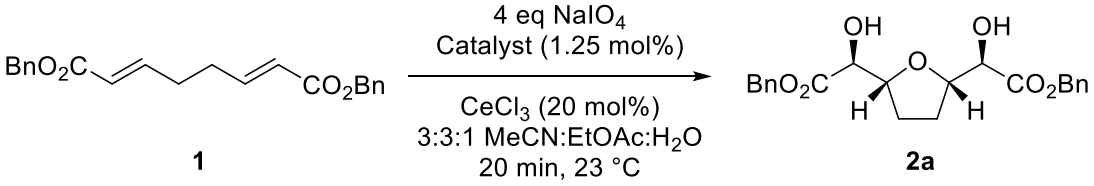
mixture was then filtered through a cotton-packed Pasteur pipette and concentrated *in vacuo* to yield a pale yellow oil (1.538 g, 55%). In a repeat of the control oxidative cyclization experiment, no conversion was observed, indicating that residual Ru contamination is sufficiently low. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.40 – 7.29 (m, 10H), 6.98 (d, *J* = 15.7 Hz, 2H), 5.90 (d, *J* = 15.6 Hz, 2H), 5.18 (s, 4H), 2.41 – 2.34 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 147.7, 136.1, 128.7, 128.4, 128.4, 122.1, 66.3, 30.6. HRMS (FAB^+): *m/z* calculated for $[C_{22}H_{22}O_4+H]^+$: 351.1596, found: 351.1581.



(2Z,6E)-8-ethoxy-8-oxo octa-2,6-dien-1-yl benzoate: Synthesized by combining the crude material from 5 optimization runs of the Z-selective metathesis procedure (see General method D) and purified by column chromatography (2% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.07 – 8.01 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 6.95 (dt, *J* = 15.7, 6.6 Hz, 1H), 5.84 (dt, *J* = 15.7, 1.5 Hz, 1H), 5.75 – 5.64 (m, 2H), 4.86 (dd, *J* = 6.4, 0.9 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.41 – 2.27 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 166.6, 147.8, 133.6, 133.1, 130.3, 129.8, 128.5, 124.8, 122.2, 60.8, 60.4, 32.0, 26.2, 14.4. HRMS (ES^+): *m/z* calculated for $[C_{17}H_{20}O_4+H]^+$: 288.1362, found: 288.1371.

ii) General procedures

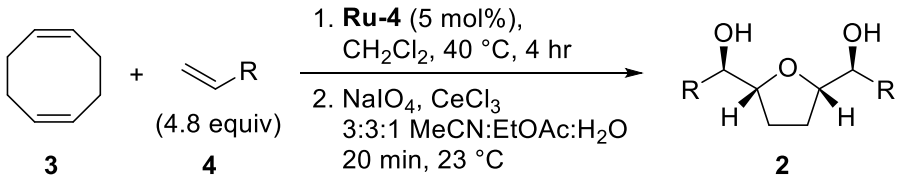
General procedure A – Optimization of oxidative cyclization conditions (Table 1):



1 **2a**

To a round bottom flask charged with $NaIO_4$ (85.6 mg, 0.40 mmol, 4 eq) was added $CeCl_3 \cdot 7H_2O$ (7.5 mg, 0.02 mmol, 0.2 eq) in H_2O (0.33 mL). To the suspension was added MeCN (1.0 mL) followed by the appropriate ruthenium catalyst (1.25 mol%) in EtOAc (0.5 mL). Finally, bisacrylate **1** (35.0 mg, 0.1 mmol, 1 eq) dissolved in EtOAc (0.5 mL) was added, and the mixture was stirred vigorously at ambient temperature. After 20 minutes, the mixture was quenched with 2 mL of saturated $Na_2S_2O_3$. The mixture was extracted with EtOAc (3 x 5 mL) and the combined organic extracts were concentrated *in vacuo*. Mesitylene (27.8 µL, 0.2 mmol, 2 eq) was added as an internal NMR standard. The crude mixture was then dissolved in $CDCl_3$ and analyzed by ^1H NMR (8 scans, 25 s relaxation delay).

General procedure B – Tandem ring opening cross metathesis – oxidative cyclization (Table 2):

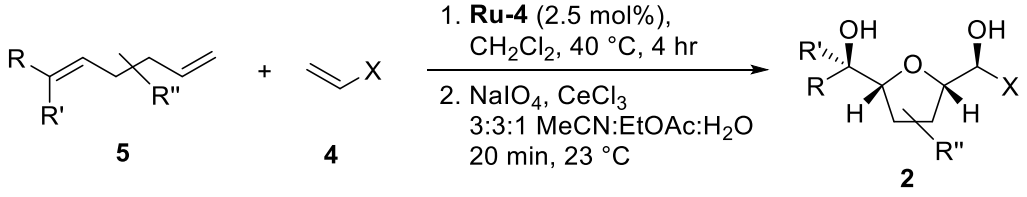


3 **4** **2**

A 25 mL 2-neck round bottom flask was charged with **Ru-4** (7.8 mg, 0.0125 mmol, 0.05 eq) and equipped with a Teflon-coated stir bar and a water-cooled reflux condenser. The flask and condenser were evacuated and refilled with Ar twice. CH_2Cl_2 (2.5 mL) was then added, followed by 1,5-cyclooctadiene (**3**) (30.7 µL, 0.25 mmol, 1 eq) and the appropriate acrylate (1.20 mmol, 4.8 eq). The resulting mixture was heated at reflux under a flow of Ar for 4 hr, and then cooled to ambient temperature.

Meanwhile, a separate round bottom flask was charged with $NaIO_4$ (513 mg, 2.4 mmol, 2 times the total expected amount of olefins after the metathesis step). $CeCl_3 \cdot 7H_2O$ (44.7 mg, 0.12 mmol) in H_2O (2 mL) was added, followed by MeCN (6 mL). EtOAc (6 mL) was added to the crude metathesis mixture, and this solution was then transferred to the oxidant mixture. This resulting brown heterogeneous mixture was stirred vigorously for 20 minutes, and then quenched with saturated $Na_2S_2O_3$ (20 mL). The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*. The title compound was then purified by column chromatography.

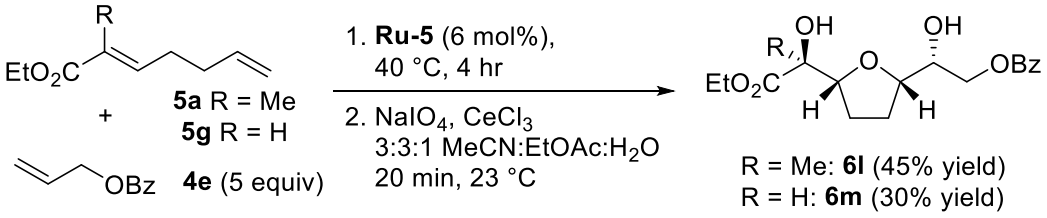
General procedure C – Tandem cross metathesis – oxidative cyclization (Table 3):



A 25 mL 2-neck round bottom flask was charged with **Ru-4** (7.8 mg, 0.0125 mmol, 0.025 eq) and equipped with a Teflon-coated stir bar and a water-cooled reflux condenser. The flask and condenser were evacuated and refilled with Ar twice. CH_2Cl_2 (2.5 mL) was then added, followed by the appropriate diene (**5**) (0.50 mmol, 1 eq) and the appropriate terminal olefin (**4**) (0.60 mmol, 1.2 eq, unless otherwise specified). The resulting mixture was heated at reflux under a flow of Ar for 4 hr, and then cooled to ambient temperature.

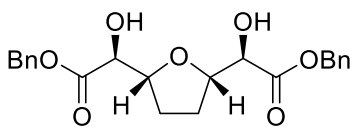
Meanwhile, a separate round bottom flask was charged with $NaIO_4$ (471 mg, 2.2 mmol, 2 times the total expected amount of olefins after the metathesis step). $CeCl_3 \cdot 7H_2O$ (41 mg, 0.11 mmol) in H_2O (2 mL) was added, followed by MeCN (6 mL). EtOAc (6 mL) was added to the crude metathesis mixture, and this solution was then transferred to the oxidant mixture. This resulting brown heterogeneous mixture was stirred vigorously for 20 minutes, and then quenched with saturated $Na_2S_2O_3$ (20 mL). The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*. The title compound was then purified by column chromatography.

General procedure D – Tandem Z-selective cross metathesis – oxidative cyclization (Scheme 2):



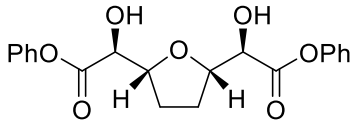
In a nitrogen filled glove box, a solution of allyl benzoate (81.1 mg, 0.5 mmol, 5.0 equiv) in THF or 2-MeTHF (50 µL) was added to the diene substrate (0.1 mmol, 1.0 equiv) in a 8 mL vial. A solution of **Ru-5** (0.006 mmol, 4.05 mg in 50 µL THF or Me-THF) was added to the vial. The vial was capped with a septum cap, and removed from the glove box. An argon inlet and outlet connected to an oil bubbler were connected. The argon flow rate was set at one bubble per second. The solution was then heated in an oil bath with stirring at 40 °C for 4 hr, and then cooled to ambient temperature. Meanwhile in a separate round bottom flask a solution of $CeCl_3 \cdot 7H_2O$ (14.9 mg, 0.04 mmol) in distilled H_2O (667 µL) was added to $NaIO_4$ (171 mg, 0.8 mmol, 2.0 equiv relative to the cross metathesis products at full conversion). MeCN (2 mL) was added at room temperature. The crude metathesis mixture was then added using EtOAc (3 x 667 µL) to rinse the flask and ensure complete transfer. The mixture was vigorously stirred at room temperature for 20 min and then quenched with 2 mL of a saturated $Na_2S_2O_3$ solution. The mixture was extracted with EtOAc (4 x 10 mL), and then concentrated under reduced pressure. The crude residue was suspended in Et_2O, in which the 1,2-diol byproduct (from allyl benzoate homodimerization and then dihydroxylation) is poorly soluble. The liquid phase was collected by pipette and concentrated, and the title compound was purified by thin layer chromatography.

iii) Product Characterization



2a

(**2a**): Synthesized according to General Procedure B using benzyl acrylate (184 µL, 1.20 mmol). The title compound was isolated by column chromatography (35-50% EtOAc in hexanes), and impure fractions were repurified using preparatory TLC (40% EtOAc in hexanes) to yield a clear oil (99.1 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 10H), 5.24 (d, J = 12.3 Hz, 2H), 5.19 (d, J = 12.3 Hz, 2H), 4.48-4.40 (m, 2H), 4.17 (d, J = 1.9 Hz, 2H), 3.86 (br s, 2H), 2.30-2.15 (m, 2H), 2.10-1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 135.3, 128.6, 128.4, 128.2, 80.5, 73.5, 67.3, 28.1; HRMS (FAB+): m/z calculated for $[C_{22}H_{24}O_7+H]^+$: 401.1600, found: 401.1580.



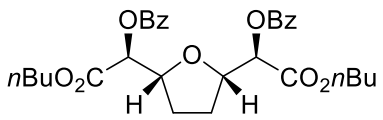
2b

(2b): For Table 2, entry 2, the title compound was synthesized according to General Procedure B using phenyl acrylate (165 µL, 1.20 mmol). Compound **2b** was isolated by two iterations of column chromatography (35-50% EtOAc in hexanes), to yield a white solid (106.4, 57%). For Table 2, entry 3, polybutadiene (M_n = 3000, 27.1 mg, 0.25 mmol) was used in place of 1,5-cyclooctadiene, and the product was isolated by column chromatography (30-40% EtOAc in hexanes) and trituration with ether to yield a white solid (65.7 mg, 35%). See below for a procedure on 5.0 mmol scale. Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a solution of **2b** in EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 4H), 7.24-7.20 (m, 2H), 7.09-7.06 (m, 4H), 4.70-4.64 (m, 2H), 4.42 (d, *J* = 1.9 Hz, 2H), 3.90 (br s, 2H), 2.42-2.34 (m, 2H), 2.22-2.12 (m, 2H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 171.5, 150.5, 129.5, 126.1, 121.3, 80.8, 73.6, 28.0; HRMS (FAB+): m/z calculated for $[C_{20}H_{20}O_7+H]^+$: 373.1287, found: 373.1289.

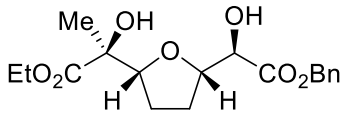
Procedure for 2.5 mmol scale reaction: A 100 mL 2-neck round bottom flask was charged with **Ru-4** (78 mg, 0.125 mmol, 0.05 eq) and equipped with a Teflon-coated stir bar and a water-cooled reflux condenser. The flask and condenser were evacuated and refilled with Ar twice. CH_2Cl_2 (12.5 mL) was then added, followed by 1,5-cyclooctadiene (307 µL, 2.5 mmol, 1 eq) and phenyl acrylate (1.65 mL, 12.0 mmol, 4.8 eq). The resulting mixture was heated at reflux under a flow of Ar for 4 hr, and then cooled to ambient temperature.

Meanwhile, a separate round bottom flask was charged with $NaIO_4$ (3.85 mg, 18 mmol, 1.5 times the total expected amount of olefins after the metathesis step). $CeCl_3$•$7H_2O$ (335.3 mg, 0.9 mmol) in H_2O (10 mL) was added, followed by MeCN (30 mL). EtOAc (30 mL) was added to the crude metathesis mixture, and this solution was then transferred to the oxidant mixture. This resulting brown heterogeneous mixture was stirred vigorously for 20 minutes, and then quenched with saturated $Na_2S_2O_3$ (30 mL). The mixture was extracted with EtOAc (3 x 100 mL) and the combined organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*. The title compound was then purified by column chromatography (30-35% EtOAc in hexanes) followed by trituration with ether to yield 964.2 mg (52%).



2c

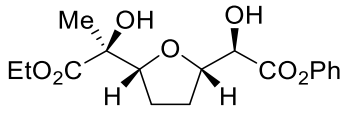
(2c): Synthesized according to General Procedure B using *n*-butyl acrylate (164 µL, 1.20 mmol). The THF diol was purified by column chromatography (30-40% EtOAc in hexanes), however inseparable impurities remained. This material was dissolved in CH_2Cl_2 (2.5 mL) and triethylamine (0.348 mL, 2.5 mmol) and benzoyl chloride (0.173 mL, 1.5 mmol) were then added. The solution was stirred at ambient temperature for 2 hours. The crude mixture was diluted with EtOAc (50 mL), washed with NH_4Cl (30 mL) and brine (30 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The title compound was isolated by column chromatography (15-20% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.4, 1.3 Hz, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.30 (dd, *J* = 8.2, 7.4 Hz, 4H), 5.33 (d, *J* = 4.5 Hz, 2H), 4.67-4.60 (m, 2H), 4.15 (t, *J* = 6.7 Hz, 4H), 2.14-2.10 (m, 4H), 1.62-1.52 (m, 4H), 1.35-1.24 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.3, 133.3, 130.0, 129.1, 128.3, 78.5, 74.6, 65.4, 30.4, 27.7, 18.9, 13.6; HRMS (FAB+): m/z calculated for $[C_{30}H_{36}O_9+H]^+$: 541.2437, found: 541.2423.



6a

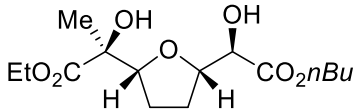
(6a): Synthesized according to General Procedure C with diene **5a** (84.1 mg, 0.5 mmol) and benzyl acrylate (92 µL, 0.6 mmol). The title compound was purified by column chromatography (25-35% EtOAc in hexanes) to yield a clear oil (114.9 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 5.20 (s, 2H), 4.44 (ddd, *J* = 8.0, 4.6, 1.8 Hz, 1H), 4.24 (t, *J* = 7.2 Hz, 1H), 4.21 (qd, *J* = 7.1, 5.6 Hz, 2H), 4.13

(s, 1H), 4.07 (br s, 2H), 2.23-2.12 (m, 2H), 2.07-1.99 (m, 1H), 1.99-1.91 (m, 1H), 1.30 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 172.6, 135.4, 128.6, 128.2, 110.0, 84.1, 80.5, 76.7, 73.8, 67.1, 62.0, 28.1, 25.9, 21.9, 14.1; HRMS (FAB+): m/z calculated for $[C_{18}H_{24}O_7+H]^+$: 353.1600; found: 353.1613.



6b

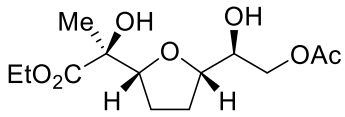
(6b): Synthesized according to General Procedure C with diene **5a** (84.1 mg, 0.5 mmol) and phenyl acrylate (83 µL, 0.6 mmol). The title compound was purified by column chromatography (30-40% EtOAc in hexanes) to yield a clear oil (111.6 mg, 66%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.4, 7.5 Hz, 1H), 7.22 (tt, *J* = 7.2, 1.3 Hz, 1H), 7.08 (dd, *J* = 8.6, 1.1 Hz, 1H), 4.62 (ddd, *J* = 8.0, 3.9, 1.8 Hz, 1H), 4.35-4.26 (m, 3H), 4.23 (qd, *J* = 7.1, 1.5 Hz, 2H), 4.04 (br s, 1H), 2.30-2.17 (m, 2H), 2.17-2.07 (m, 1H), 2.02-1.96 (m, 1H), 1.32 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 171.5, 150.6, 129.4, 126.0, 121.4, 84.1, 80.81, 76.5, 74.4, 62.2, 28.1, 25.9, 22.0, 14.1; HRMS (FAB+): m/z calculated for $[C_{17}H_{22}O_7+H]^+$: 339.1444; found: 339.1454.



6c

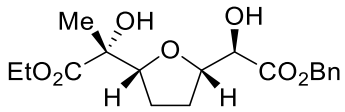
(6c): Synthesized according to General Procedure C with diene **5a** (84.1 mg, 0.5 mmol) and *n*-butyl acrylate (86 µL, 0.6 mmol). The title compound was purified by column chromatography (30-35% EtOAc in hexanes) to yield a clear oil (96.1 mg,

60%). ^{1}H NMR (400 MHz, C_6D_6) δ 4.47 (br s, 1H), 4.28 (ddd, *J* = 7.6, 4.7, 1.9 Hz, 2H), 4.13 (dd, *J* = 7.1, 6.2 Hz, 1H), 4.08-3.92 (m, 5H), 2.15-2.02 (m, 2H), 1.58-1.41 (m, 2H), 1.41-1.33 (m, 2H), 1.19 (s, 3H), 1.15 (sex, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 175.5, 172.9, 84.6, 81.1, 76.9, 73.9, 65.2, 61.7, 30.8, 28.3, 26.1, 21.9, 19.3, 14.1, 13.8; HRMS (FAB+): m/z calculated for $[C_{15}H_{26}O_7+H]^+$: 319.1757; found: 319.1751.



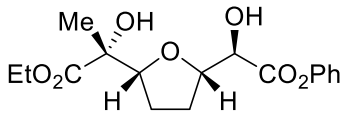
6d

(**6d**): Synthesized according to General Procedure C modified with the following amounts: diene **5a** (84.1 mg, 0.5 mmol), cis-acetoxy-2-butene **4d** (199 µL, 1.25 mmol), **Ru-4** (15.7 mg, 0.025 mmol, 5 mol%) and CH_2Cl_2 (2.5 mL) for the metathesis step. For the oxidative cyclization step: $NaIO_4$ (856 mg, 4.0 mmol), $CeCl_3$•$7H_2O$ (74.5 mg, 0.2 mmol), MeCN (11 mL), EtOAc (11 mL), H_2O (3.6 mL). The title compound was purified by column chromatography (50-55% EtOAc in hexanes) to yield a clear oil (86.3 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34-4.21 (m, 3H), 4.11 (s, 1H), 4.10 (d, *J* = 0.6 Hz, 1H), 4.05 (ddd, *J* = 7.7, 5.0, 2.9 Hz, 1H), 3.82 (s, 1H), 3.70-3.65 (m, 1H), 3.29 (d, J = 7.9 Hz, 1H), 2.08 (s, 3H), 2.20-1.90 (m, 4H), 1.31 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 171.3, 83.9, 79.7, 76.5, 72.3, 66.7, 62.4, 28.5, 25.6, 22.5, 21.1, 14.3. HRMS (FAB+): m/z calculated for $[C_{13}H_{22}O_7+H]^+$: 291.1444; found: 291.1432.



6e

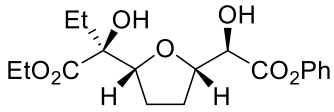
(**6e**): Synthesized according to General Procedure C with diene **5b** (84.1 mg, 0.5 mmol) and benzyl acrylate (92 µL, 0.6 mmol). The title compound was purified by column chromatography (33-40% EtOAc in hexanes) to yield a clear oil (122.1 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5H), 5.30 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.3 Hz, 1H), 4.52 (ddd, *J* = 8.0, 5.3, 1.5 Hz, 1H), 4.24 (qd, *J* = 7.2, 1.5 Hz, 1H), 4.16 (t, *J* = 7.0 Hz, 1H), 4.13 (s, 1H), 3.59 (br s, 2H), 2.22-2.12 (m, 1H), 2.09-2.00 (m, 1H), 2.00-1.91 (m, 1H), 1.87-1.78 (m, 1H), 1.45 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 172.6, 135.6, 128.5, 128.3, 128.2, 83.5, 80.6, 76.5, 73.9, 66.9, 62.1, 27.9, 26.4, 23.7, 14.1; HRMS (FAB+): m/z calculated for $[C_{18}H_{24}O_7+H]^+$: 353.1600; found: 353.1595.



6f

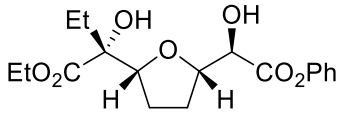
(**6f**): Synthesized according to General Procedure C with diene **5b** (84.1 mg, 0.5 mmol) and phenyl acrylate (83 µL, 0.6 mmol). The title compound was purified by column chromatography (35-40% EtOAc in hexanes) to yield a clear oil (123.8 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 4.69 (ddd, *J* = 8.1, 5.0, 1.8 Hz, 1H), 4.46 (br s, 1H), 4.33 (s, 1H), 4.30-4.20 (m, 3H), 3.62 (br s, 1H), 2.32-2.22 (m, 1H), 2.18-2.07 (m, 1H), 2.06-1.95 (m, 1H), 1.93-1.83 (m, 1H), 1.52 (s, 3H), 1.30 (td, *J* = 7.2, 0.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 171.5, 150.7, 129.5, 125.9, 121.4, 83.5,

80.9, 76.5, 74.2, 62.3, 28.0, 26.5, 23.8, 14.1; HRMS (FAB+): m/z calculated for $[C_{17}H_{22}O_7+H]^+$: 339.1444; found: 339.1448.



6g

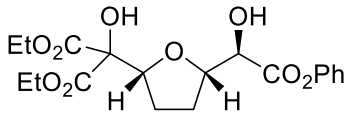
(**6g**): Synthesized according to General Procedure C with diene **5c** (91.2 mg, 0.5 mmol) and phenyl acrylate (83 µL, 0.6 mmol). The title compound was purified by column chromatography (30-40% EtOAc in hexanes) to yield a clear oil (128.7 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 4.63 (ddd, *J* = 8.0, 3.2, 1.9 Hz, 1H), 4.39 (d, *J* = 11.0 Hz, 1H), 4.33-4.29 (m, 2H), 4.26 (qd, *J* = 6.5, 1.0 Hz, 2H), 3.97 (d, *J* = 1.1 Hz, 1H), 2.30-2.07 (m, 3H), 2.01-1.93 (m, 1H), 1.77-1.67 (m, 1H), 1.59-1.48 (m, 1H), 1.28 (td, *J* = 7.2, 0.6 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 171.5, 150.7, 129.4, 125.9, 121.4, 84.0, 80.7, 80.2, 74.9, 62.2, 28.3, 28.0, 26.1, 14.2, 7.6. HRMS (FAB+): m/z calculated for $[C_{18}H_{24}O_7+H]^+$: 353.1600; found: 353.1608.



6h

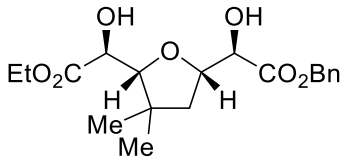
(**6h**): Synthesized according to General Procedure C with diene **5d** (91.2 mg, 0.5 mmol) and phenyl acrylate (83 µL, 0.6 mmol). The title compound was purified by two iterations of column chromatography (30-40% EtOAc in hexanes) to yield a clear oil (106.6 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.4, 7.4 Hz,

2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.13 (dd, *J* = 8.7, 1.2 Hz, 2H), 4.69 (ddd, *J* = 8.2, 4.8, 1.8 Hz, 1H), 4.57 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.35-4.22 (m, 4H), 3.60 (s, 1H), 2.31-2.22 (m, 1H), 2.18-1.94 (m, 3H), 1.90-1.76 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 171.6, 150.8, 129.6, 126.0, 121.6, 83.5, 81.1, 80.2, 74.6, 62.4, 29.9, 28.1, 26.7, 14.4, 8.0. HRMS (FAB+): m/z calculated for $[C_{18}H_{24}O_7+H]^+$: 353.1600; found: 353.1607.



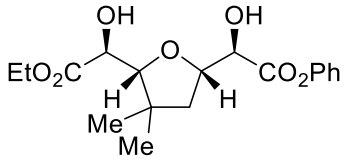
6i

(**6i**): Synthesized according to General Procedure C with diene **5e** (113.2 mg, 0.5 mmol) and phenyl acrylate (83 µL, 0.6 mmol). The title compound was purified by column chromatography (30-35% EtOAc in hexanes) to yield a clear oil (84.1 mg, 42%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.12 (dd, *J* = 8.7, 1.3 Hz, 2H), 7.06 (dd, *J* = 8.8, 7.1 Hz, 2H), 6.90 (tt, *J* = 7.3, 1.3 Hz 1H), 5.00 (t, *J* = 6.9 Hz, 1H), 4.63 (s, 1H), 4.36 (ddd, *J* = 7.5, 5.5, 1.8 Hz, 1H), 4.14 (d, *J* = 10.3 Hz, 1H), 4.06 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.97 (qd, *J* = 7.1, 1.8 Hz, 2H), 3.92-3.81 (m, 2H), 2.42-2.32 (m, 1H), 2.15-2.06 (m, 1H), 2.05-1.95 (m, 1H), 1.59-1.49 (m, 1H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 171.3, 170.0, 168.0, 151.4, 129.6, 126.0, 121.9, 82.1, 81.6, 81.3, 73.9, 63.0, 61.9, 28.1, 27.3, 13.9, 13.8. HRMS (FAB+): m/z calculated for $[C_{19}H_{24}O_9+H]^+$: 397.1498; found: 397.1480.



6j

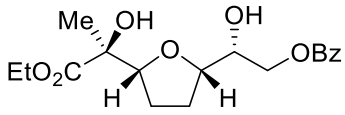
(**6j**): Synthesized according to General Procedure C with diene **5f** (91.2 mg, 0.5 mmol) and benzyl acrylate (92 µL, 0.6 mmol). The title compound was purified by column chromatography (25-30% EtOAc in hexanes) to yield a clear oil (139.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 5H), 5.34 (d, *J* = 12.3 Hz, 1H), 5.17 (d, *J* = 12.3 Hz, 1H), 4.67 (d, *J* = 11.1 Hz, 1H), 4.51 (ddd, *J* = 10.8, 6.2, 1.3 Hz, 1H), 4.30-4.10 (m, 4H), 3.94 (d, *J* = 1.6 Hz, 1H), 3.81 (br s, 1H), 2.32 (t, *J* = 11.4 Hz, 1H), 1.65 (dd, *J* = 12.1, 6.2 Hz, 1H), 1.29 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 172.5, 135.0, 128.6, 128.5, 128.3, 88.6, 78.4, 73.6, 71.9, 67.8, 61.4, 42.3, 40.9, 29.2, 22.0, 14.1; HRMS (FAB+): m/z calculated for $[C_{19}H_{26}O_7+H]^+$: 367.1757; found: 367.1751.



6k

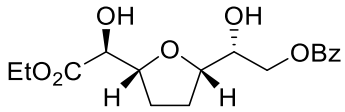
(**6k**): Synthesized according to General Procedure C with diene **5f** (91.2 mg, 0.5 mmol) and phenyl acrylate (83 µL, 0.6 mmol). The title compound was purified by two iterations of column chromatography (25-35% EtOAc in hexanes) to yield a white solid (110.6 mg, 63%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.28-7.22 (m, 1H), 7.14-7.09 (m, 2H), 4.67 (ddd, *J* = 10.8, 6.2, 1.5 Hz, 1H), 4.45 (d, *J* = 10.1 Hz, 1H), 4.41 (dd, *J* = 5.8, 1.5 Hz, 1H), 4.22 (qd, *J* = 7.2, 4.4 Hz, 2H), 4.16 (dd, *J* = 10.2, 1.7 Hz, 1H), 3.99 (d, *J* = 1.6 Hz, 1H), 3.85 (d, *J* = 5.9 Hz, 1H), 2.40

(t, *J* = 11.4 Hz, 1H), 1.73 (dd, *J* = 12.1, 6.2 Hz, 1H), 1.32 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 2H), 1.20 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 171.6, 150.6, 129.7, 126.4, 121.4, 88.7, 78.8, 73.7, 72.3, 61.7, 42.6, 41.0, 29.4, 22.3, 14.3; HRMS (FAB+): m/z calculated for $[C_{18}H_{24}O_7+H]^+$: 353.1600; found: 353.1595.



6l

(**6l**): Synthesized according to General Procedure D with diene **5a** (15.4 mg, 0.1 mmol) in MeTHF. The crude mixture was first purified by preparatory TLC (40% EtOAc in hexanes). The resulting material still contained a significant quantity of the dihydroxylated allyl benzoate dimer (2,3-dihydroxybutane-1,4-diyl dibenzoate). The impurity was precipitated with 1:1 Et_2O:Hexanes (200 µL), and the liquid was collected and concentrated *in vacuo* to yield a clear oil (16.8 mg, containing 6 mol% 1,2-diol impurity, corrected yield is 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 4.44 (dd, *J* = 11.5, 3.9 Hz, 1H), 4.33-4.20 (m, 4H), 4.14 (dt, *J* = 6.9, 4.1 Hz, 1H), 4.07 (dt, *J* = 7.1, 5.1 Hz, 1H), 3.90 (br s, 1H), 3.35 (br s, 1H), 2.17-2.06 (m, 2H), 2.02-1.90 (m, 2H), 1.32 (s, 3H), 1.30 (3, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 166.9, 133.3, 129.9, 129.9, 128.5, 83.6, 80.5, 76.3, 71.6, 66.4, 62.2, 25.9, 25.7, 22.3, 14.3. HRMS (FAB+): *m/z* calculated for $[C_{18}H_{25}O_7]^+$: 353.1600.; found: 353.1610.



6m

(**6m**): Synthesized according to General Procedure D with diene **5g** (16.8 mg, 0.1 mmol) in THF. The title compound was purified by preparatory TLC (50% EtOAc in hexanes) to yield a clear oil (10.3 mg, 30%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.45 – 7.41 (m, 2H), 4.45 – 4.40 (m, 2H), 4.34 – 4.23 (m, 3H), 4.19 (dt, *J* = 7.0, 4.0 Hz, 1H), 4.13 (d, *J* = 1.9 Hz, 1H), 4.08 (ddd, *J* = 7.3, 6.0, 4.1 Hz, 1H), 2.23 – 2.14 (m, 2H), 2.10 – 2.03 (m, 1H), 1.97 – 1.90 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 166.9, 133.3, 129.9, 129.9, 128.6, 80.7, 79.9, 73.1, 71.5, 66.4, 62.1, 27.9, 25.9, 14.3. HRMS (ES+): *m/z* calculated for $[C_{17}H_{23}O_7]^+$: 339.1410.; found: 339.1444.

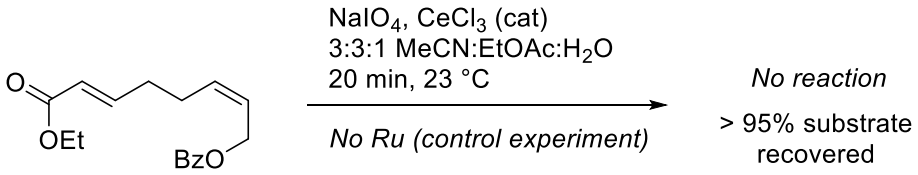
iv) Miscellaneous experiments

Optimization of ring opening cross metathesis:

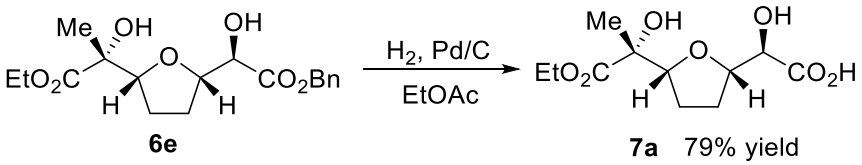
A 25 mL 2-neck round bottom flask was charged with **Ru-4** (0.02 - 0.05 eq) and equipped with a Teflon-coated stir bar and a water-cooled reflux condenser. The flask and condenser were evacuated and refilled with Ar twice. CH_2Cl_2 (2.5 mL) was then added, followed by 1,5-cyclooctadiene (**3**) (30.7 µL, 0.25 mmol, 1 eq) and methyl acrylate (1.2-1.5 mmol). The resulting mixture was heated at reflux under a flow of Ar, and aliquots were taken at various times for analysis by ^{1}H NMR (conversion calculated based on product and poly(cyclooctadiene) integrals).

Entry	Acrylate (equiv)	**Ru-4** (mol %)	Time (h)	Conversion (%)
1	1.5	2	1	72
2	1.5	2	2.5	88
3	1.5	5	1	92
4	1.5	5	2.5	98
5	1.2	2	3	75
6	1.2	2	5	81
7	1.2	5	3	98
8	1.2	5	5	99

Control experiment: Oxidation of E,Z-diene in the absence of Ru



Reaction performed according to General procedure A, with no ruthenium catalyst added. By ^{1}H NMR, no product was observed, and the substrate was recovered with >95%.

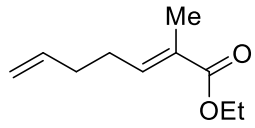


6e **7a** 79% yield

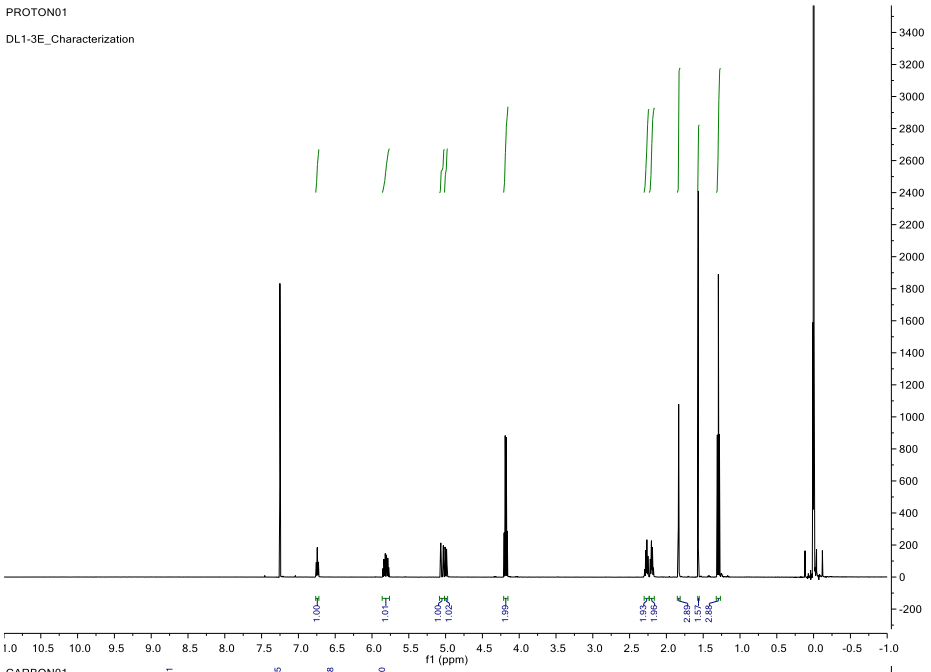
(**7a**): To a 50 mL Schlenk flask under Ar was added Pd/C (14.4 mg, 0.0136 mmol, 10%). The flask was evacuated and refilled with Ar, then EtOAc (2.7 mL) was

added. The flask was then purged with an H_2 balloon five times and allowed to stir at ambient temperature with an H_2 balloon. After 2.5 hr, the reaction was complete by TLC. The crude mixture was filtered over Celite, washed with EtOAc, and concentrated *in vacuo* to yield a clear solid (56.6 mg, 79%). A single crystal suitable for x-ray diffraction was grown by slow diffusion of pentane into a solution of **7a** in EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.0-4.0 (br s), 4.62 (ddd, *J* = 8.6, 6.9, 1.8 Hz, 1H), 4.26 (qq, *J* = 7.1, 3.6 Hz, 2H), 4.21 (dd, *J* = 7.7, 5.8 Hz, 1H), 4.14 (d, *J* = 1.8 Hz, 1H), 2.18-2.05 (m, 2H), 1.97-1.90 (m, 1H), 1.90-1.81 (m, 1H), 1.49 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $cdcl_3$) δ 175.1, 174.7, 83.1, 80.2, 77.1, 73.3, 62.7, 28.0, 26.8, 23.9, 14.3. HRMS (FAB+): *m/z* calculated for $[C_{11}H_{19}O_7]^+$: 263.1131; found: 263.1129.

3. Spectra


Me
O
OEt

5a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1.96
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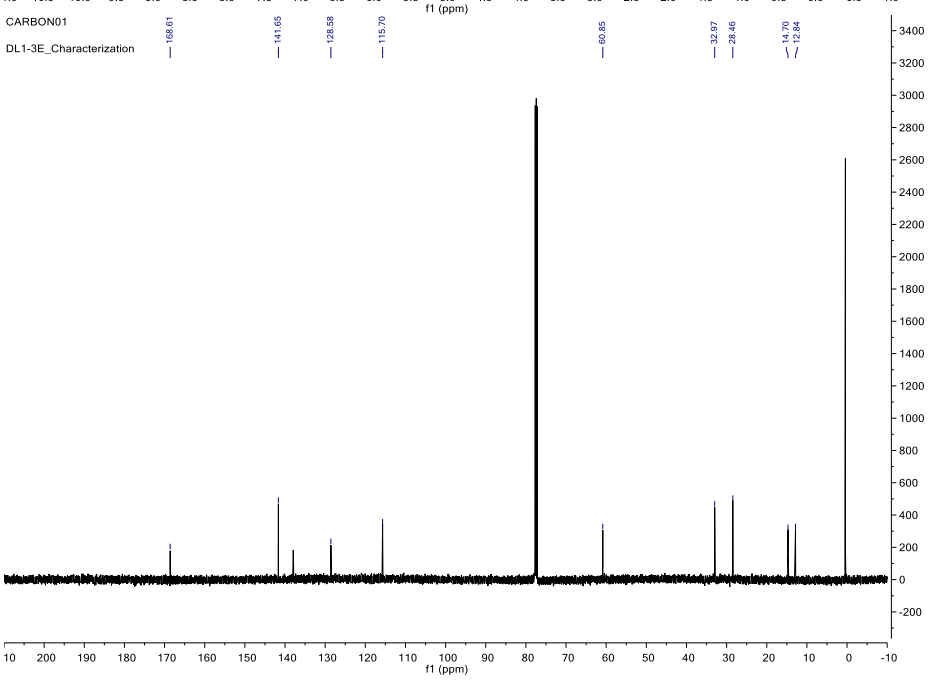
1.57
2.88
f1 (ppm)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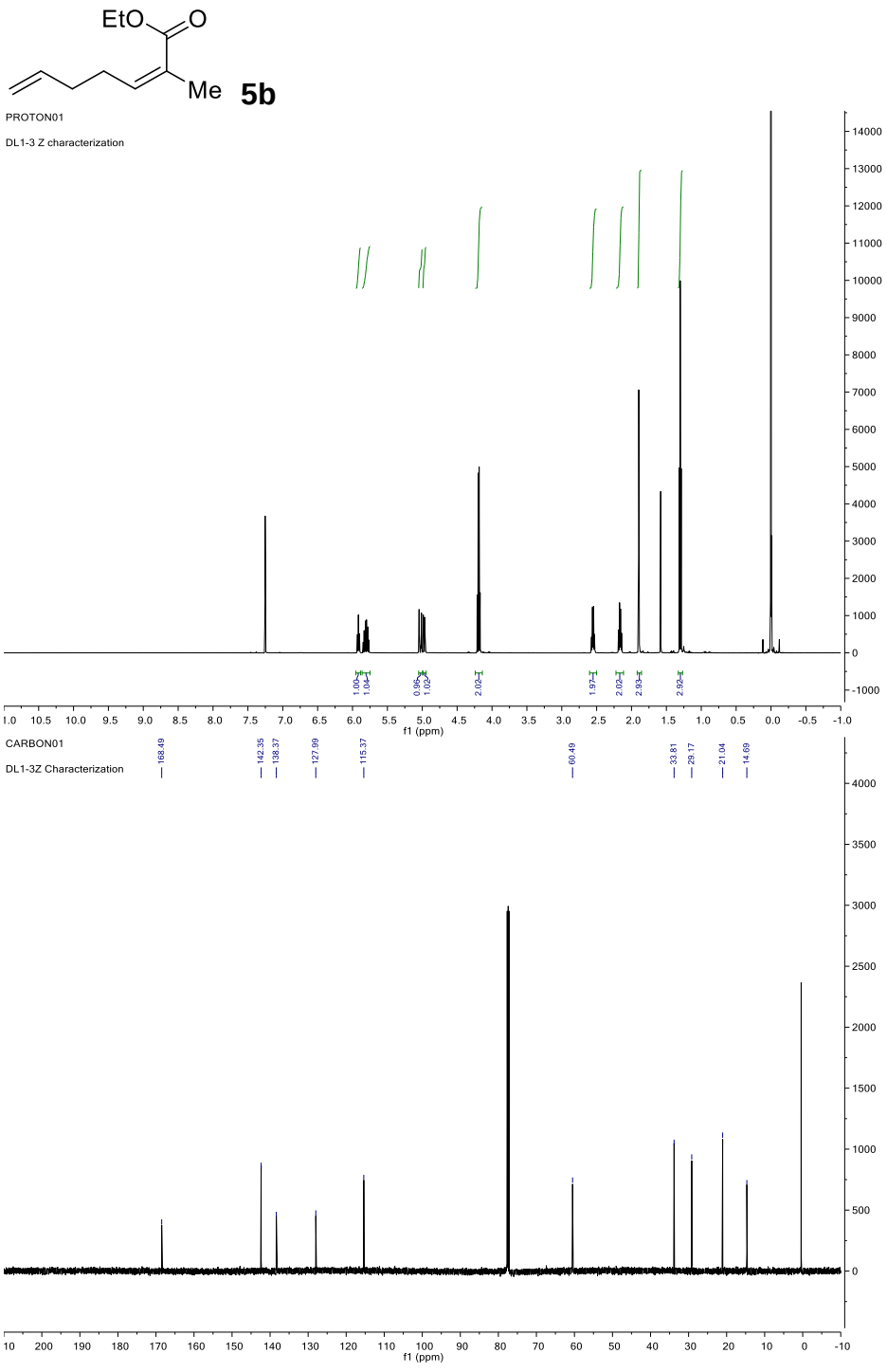
32.97
28.46
14.70
12.84
f1 (ppm)


EtO
O
Me
5b
PROTON01
DL1-3 Z characterization
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0.96
1.02
2.02
1.97
2.05
2.93
2.92
f1 (ppm)
CARBON01
DL1-3Z Characterization
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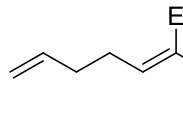
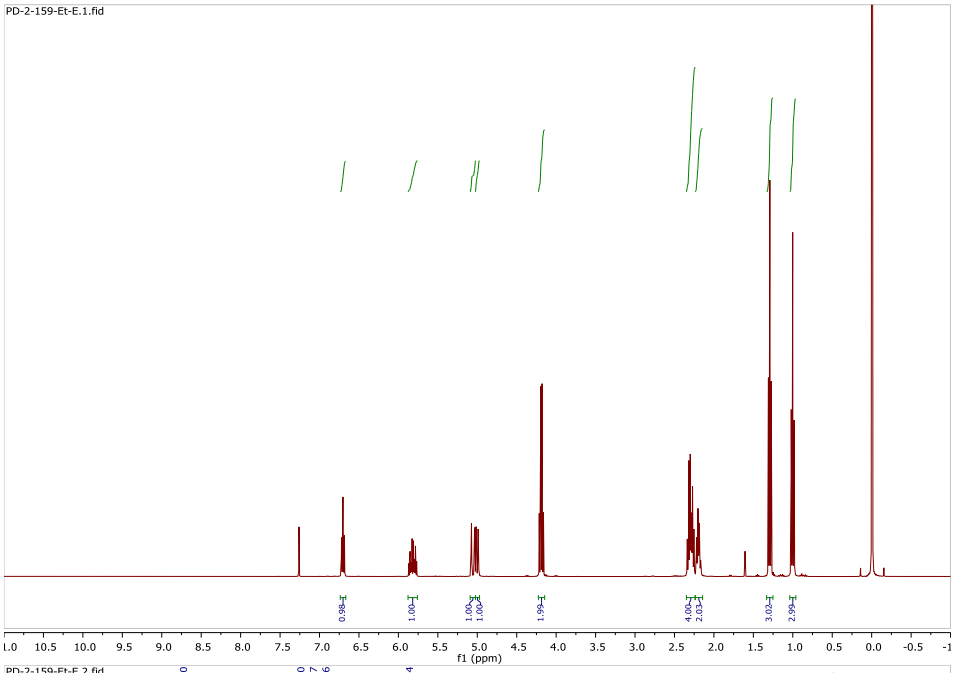
138.37
127.99
115.37
60.49
33.81
29.17
21.04
14.69
f1 (ppm)


Et
O
OEt

5c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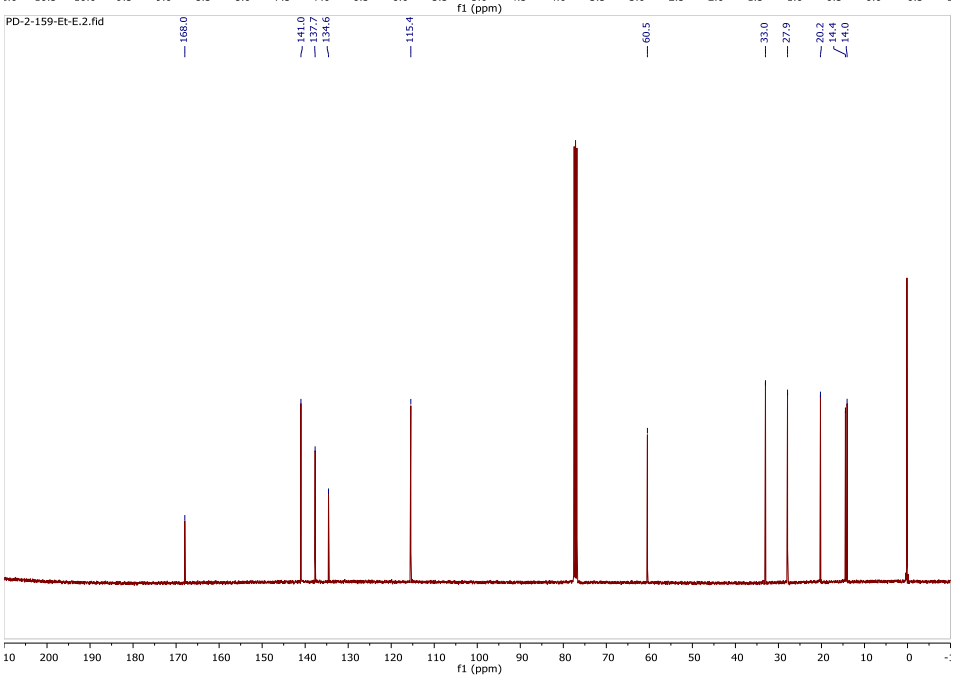
1.00
1.99
4.00
2.03
3.02
2.99
f1 (ppm)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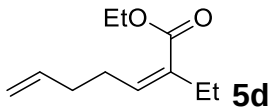
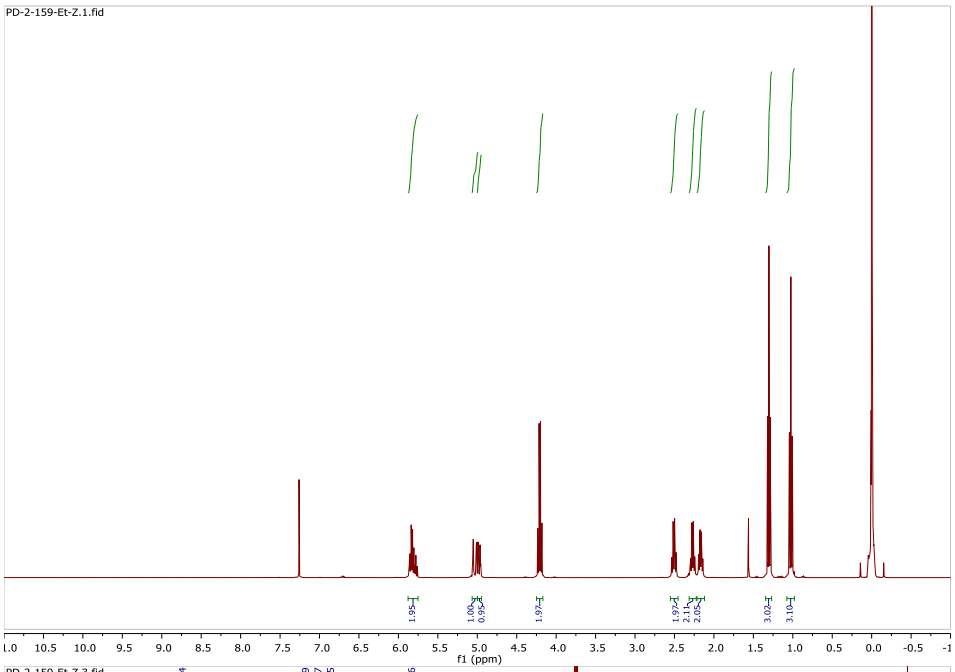
33.0
27.9
20.2
14.4
14.0
f1 (ppm)


EtO
O
Et

5d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1.97
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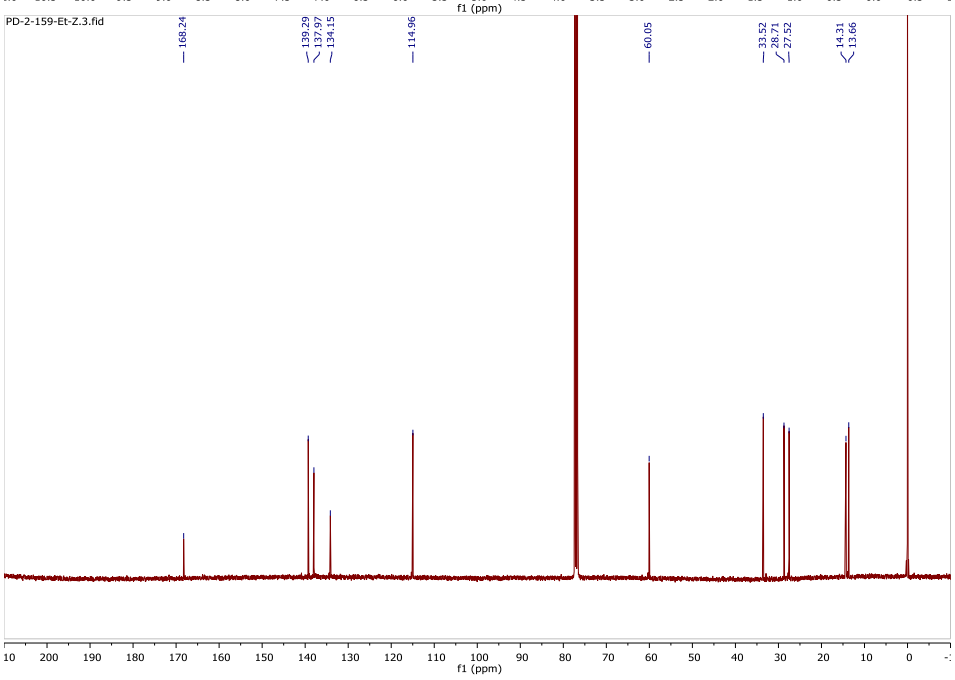
2.05
3.03
3.10
f1 (ppm)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137.97
134.15
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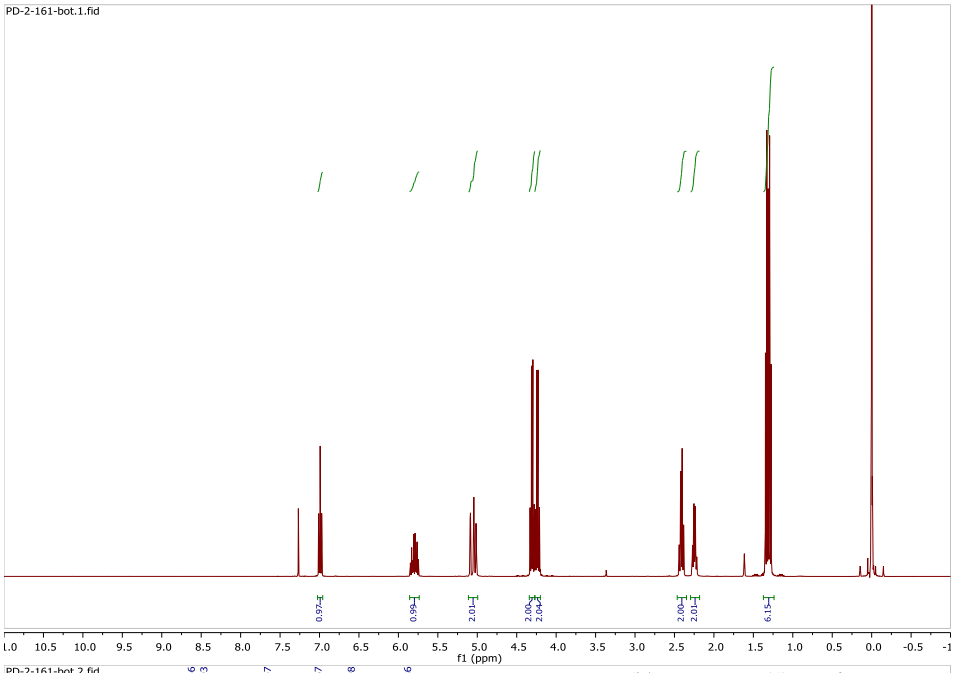
33.52
28.71
27.52
14.31
13.66
f1 (ppm)


CO2Et
CO2Et

5e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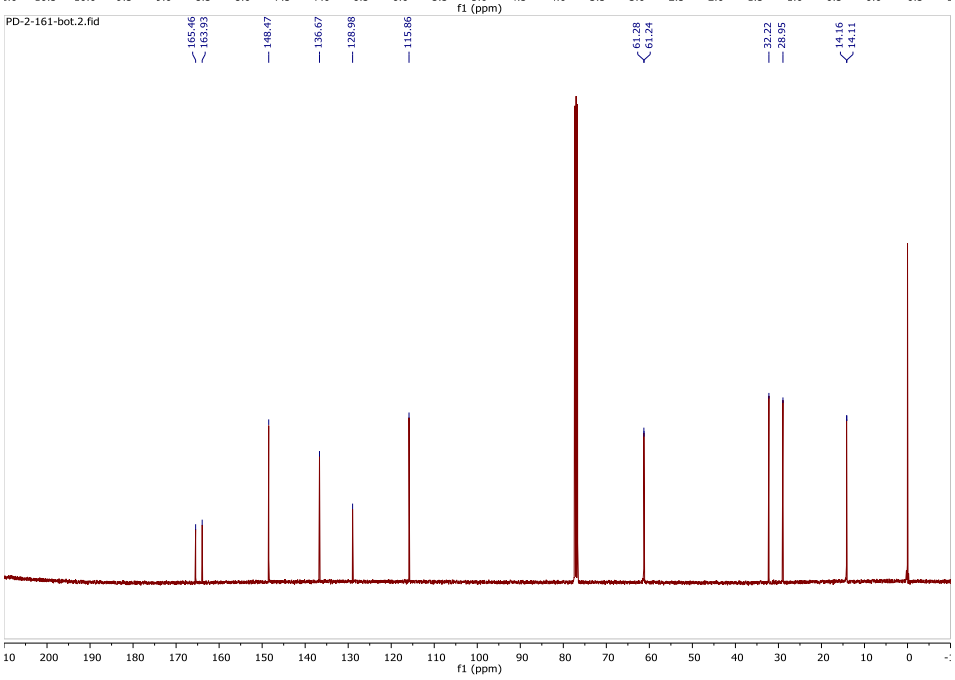
2.00
2.04
2.00
2.01
6.15
f1 (ppm)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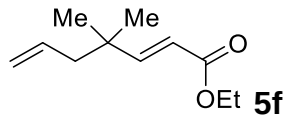
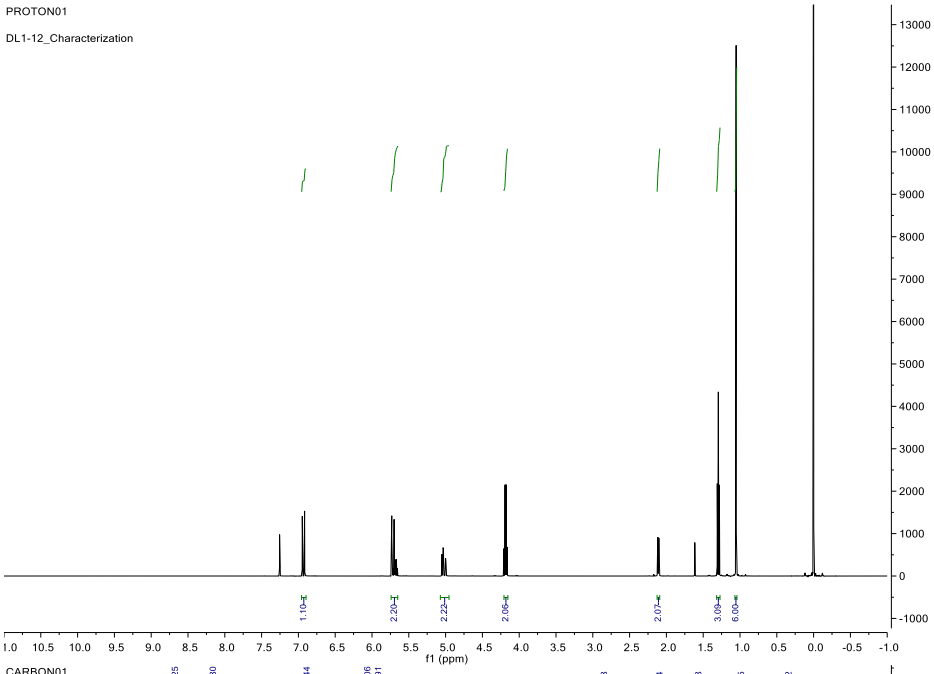
61.24
32.22
28.95
14.16
14.11
f1 (ppm)


Me
Me
O
OEt

5f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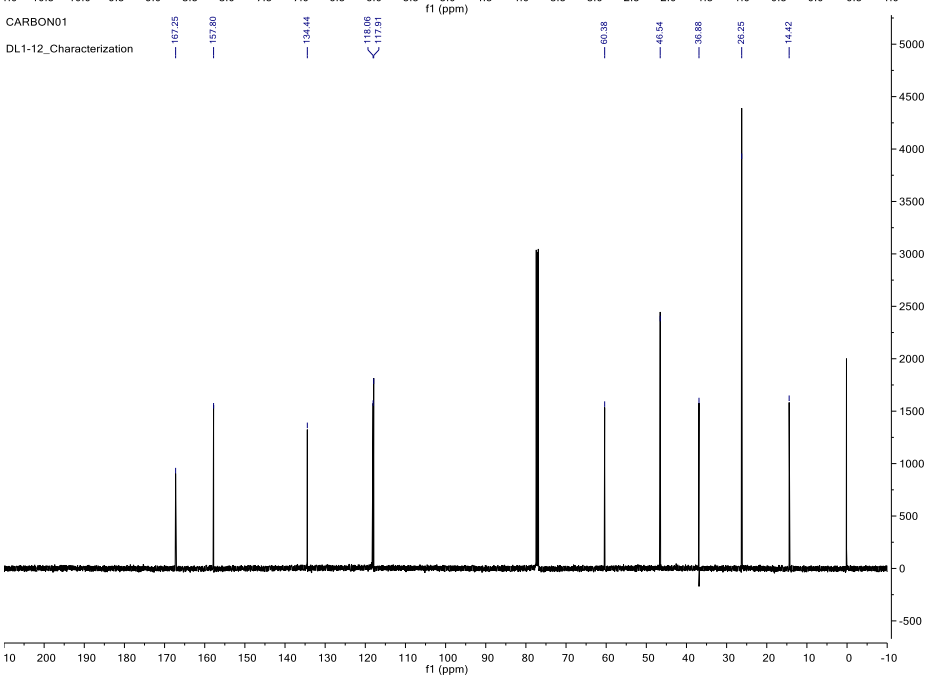
6.00
f1 (ppm)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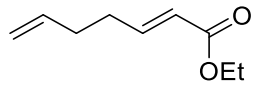
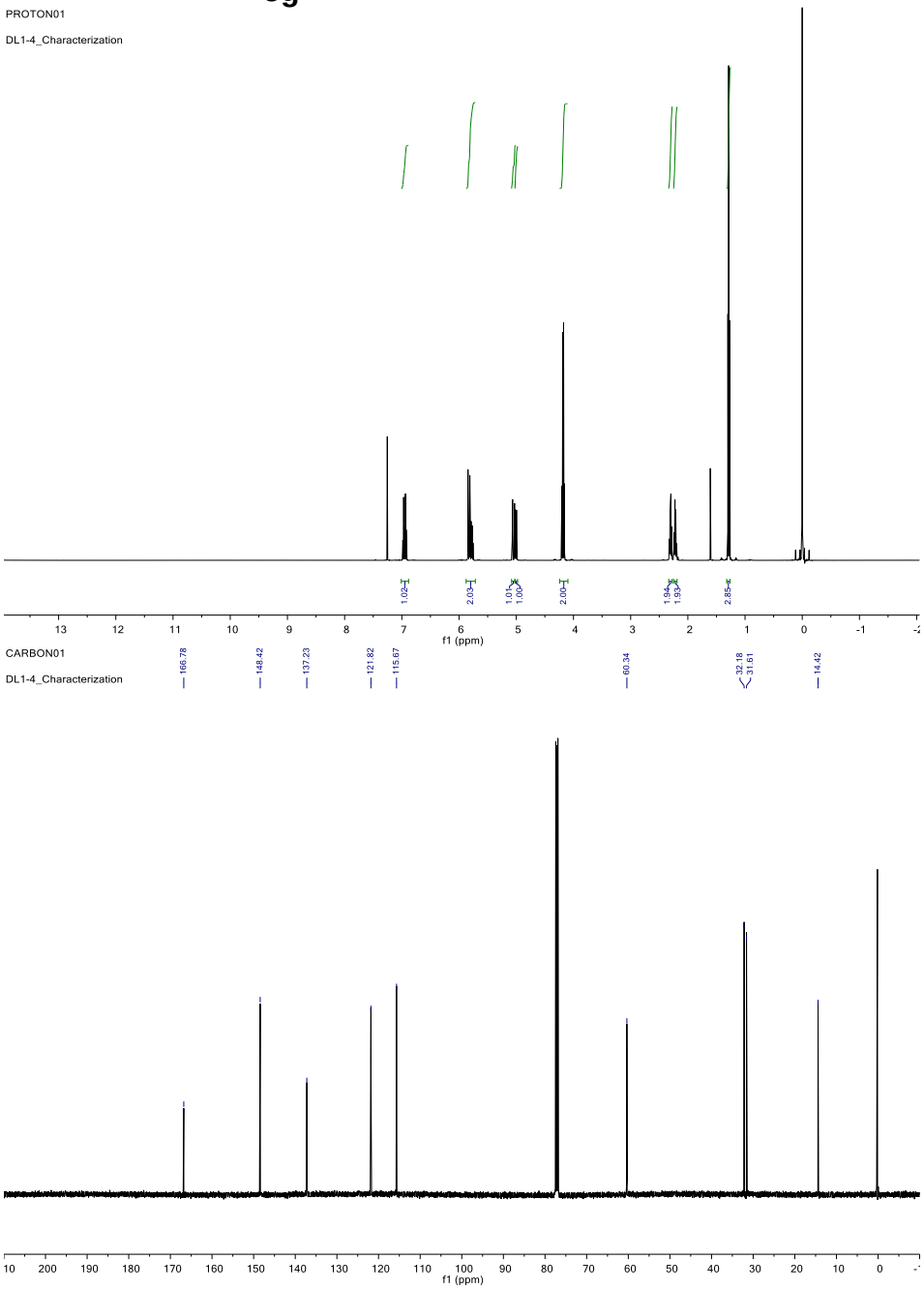
f1 (ppm)


O
OEt

5g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1.89
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f1 (ppm)
CARBON01
DL1-4_Characterization
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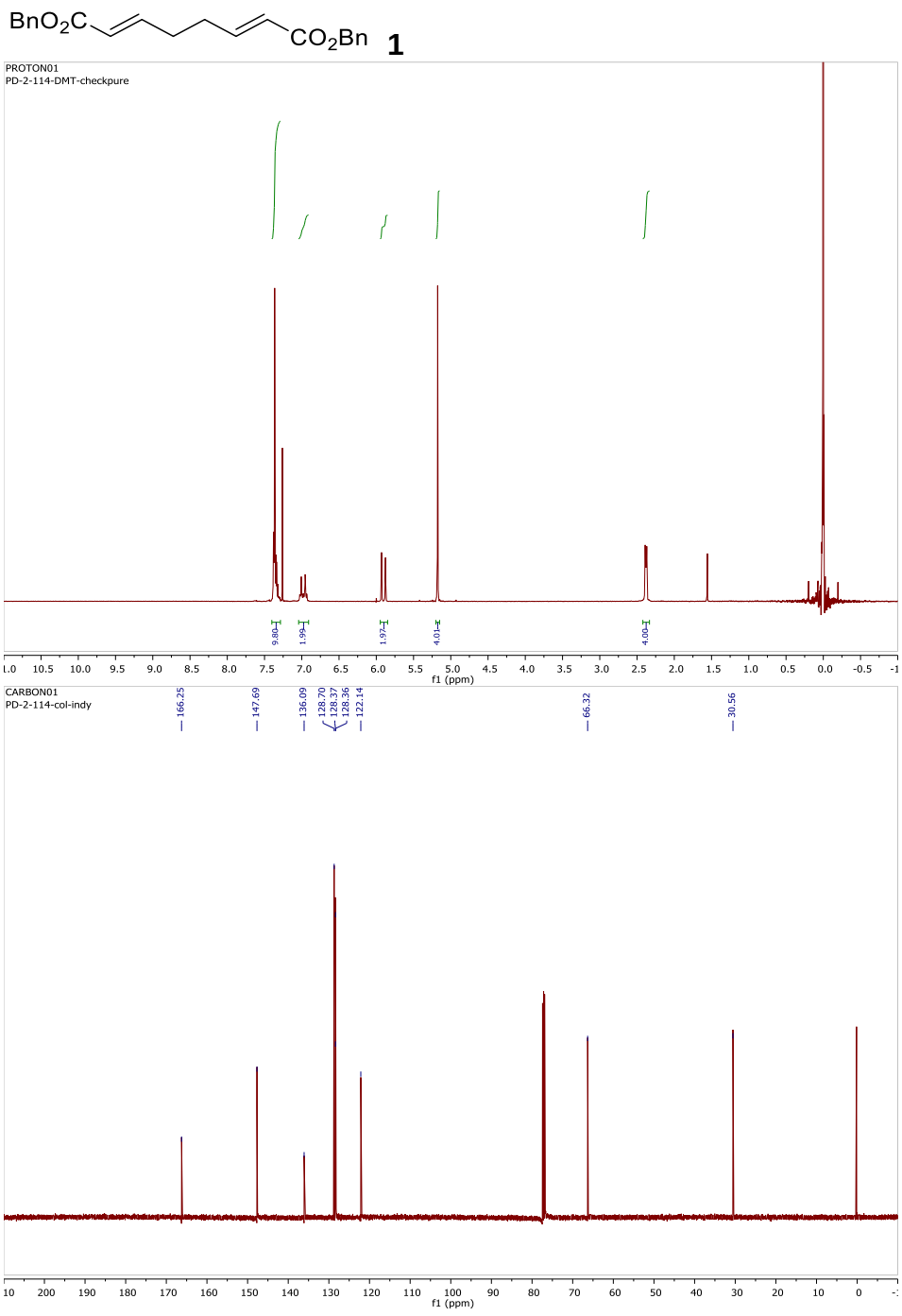
60.34
32.18
31.61
14.42
f1 (ppm)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CO2Bn
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PROTON01
PD-2-114-DMT-checkpure
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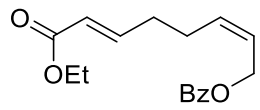
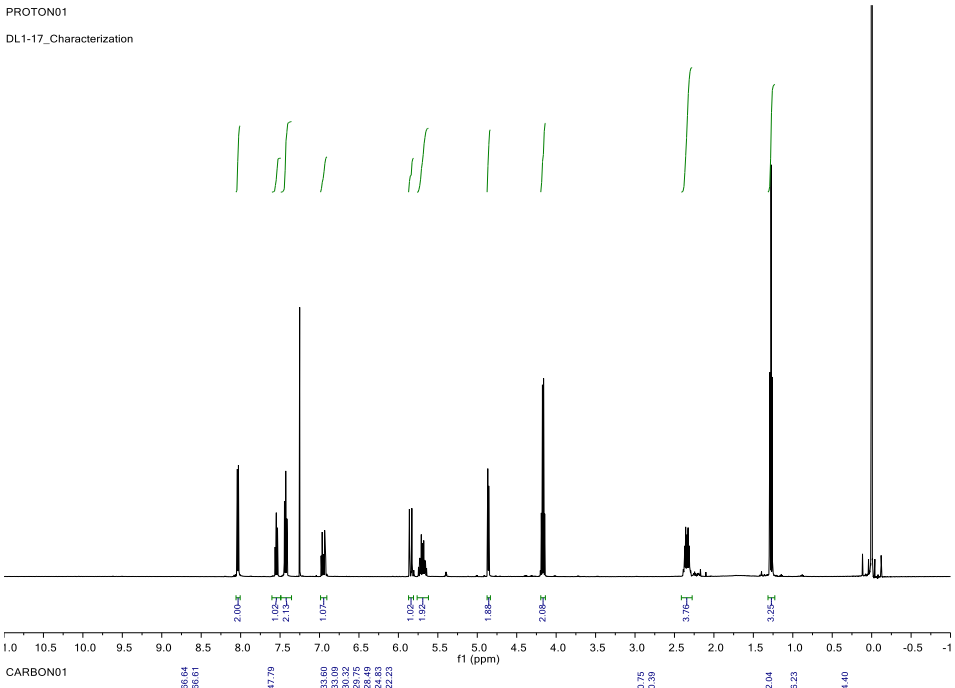
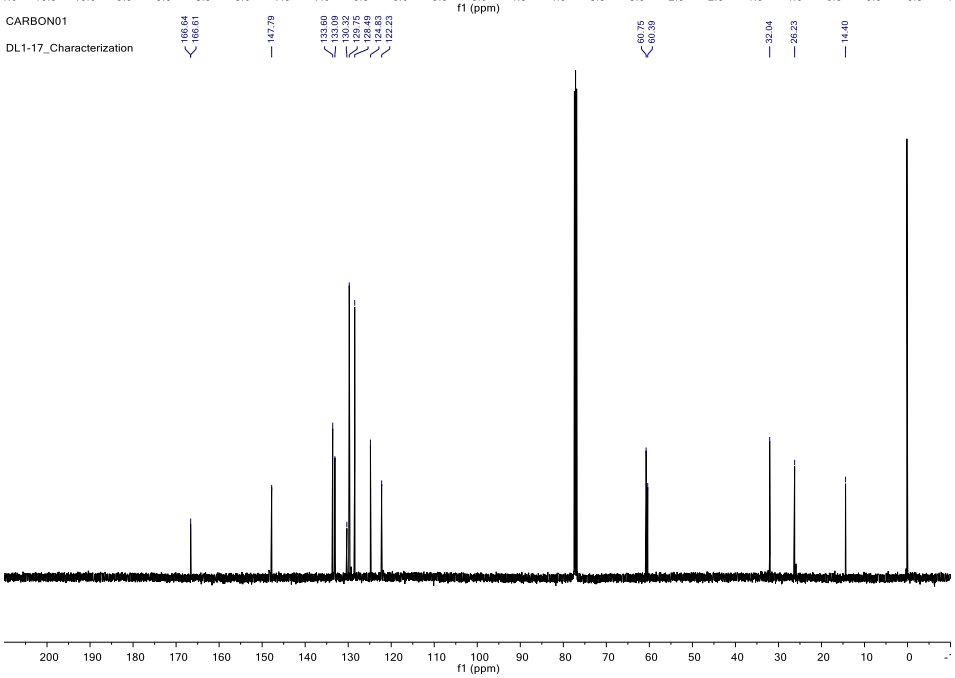
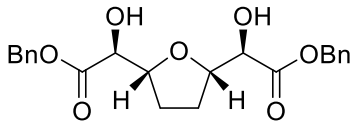
1.97
4.01
4.00
f1 (ppm)
CARBON01
PD-2-114-col-indy
166.25
147.69
136.09
128.70
128.37
128.36
122.14
66.32
30.56
f1 (ppm)

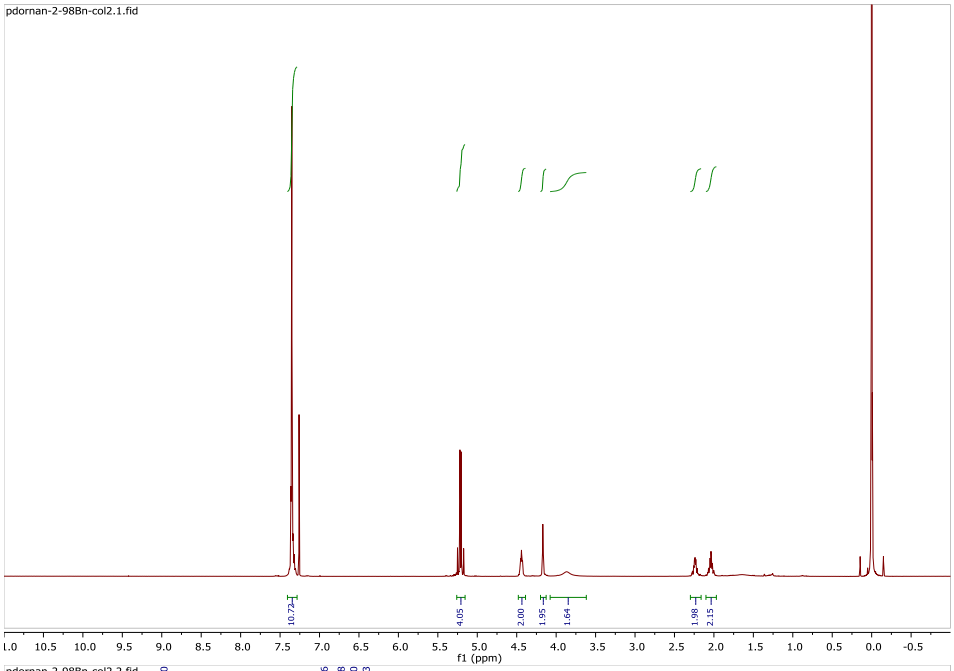

O
OEt
BzO

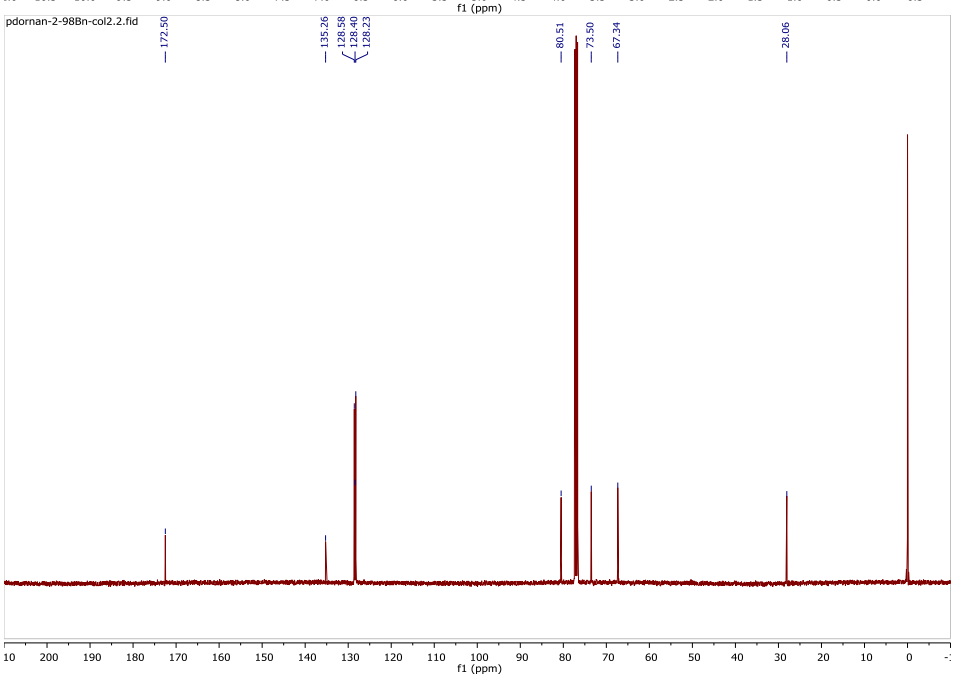

PROTON01
DL1-17_Characterization
2.00
1.02
2.13
1.07
1.02
1.92
1.88
2.08
3.76
3.25
f1 (ppm)

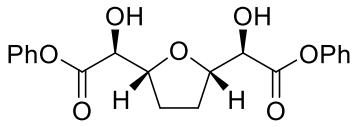

CARBON01
DL1-17_Characterization
166.64
166.61
147.79
133.60
133.09
130.32
129.75
128.49
128.43
122.23
60.75
60.39
32.04
26.23
14.40
f1 (ppm)


OH
OH
BnO
O
OBn
H
H
O
O

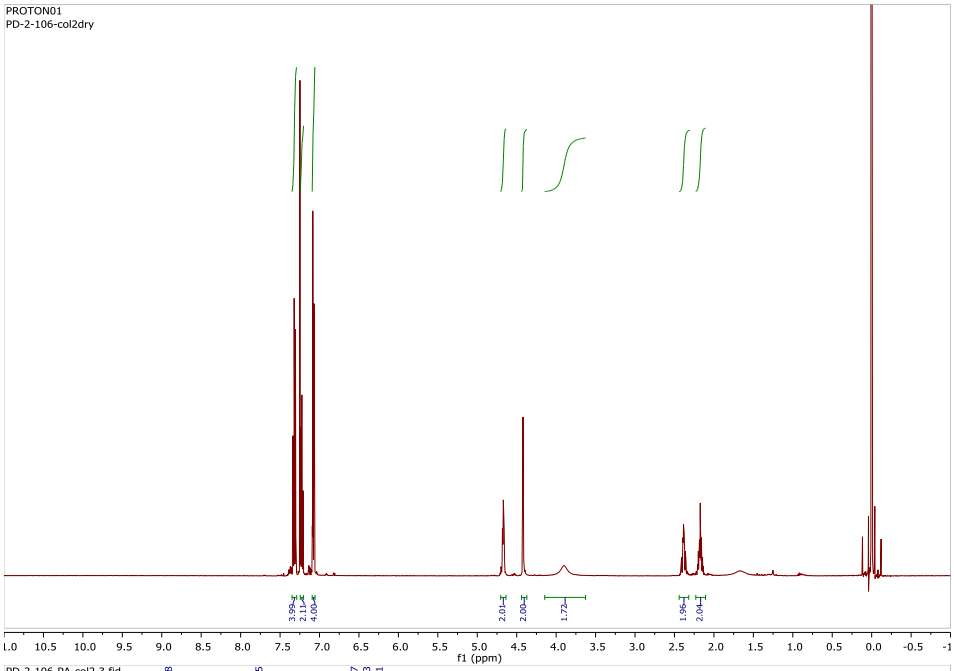
2a

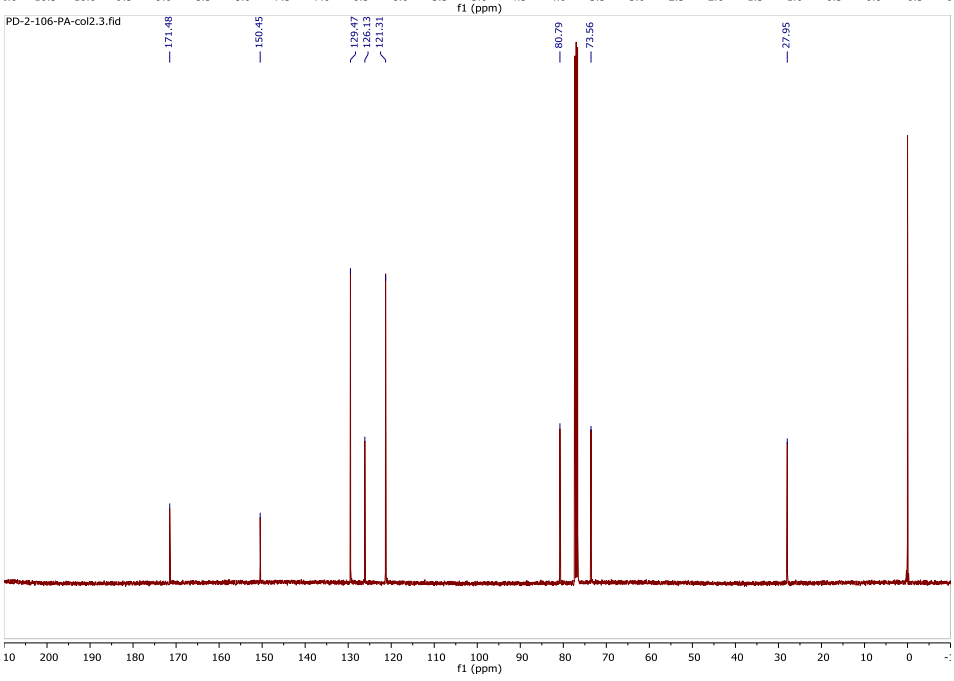

pdornan-2-98Bn-col2.1.fid
10.72
4.05
2.00
1.95
1.64
1.98
2.15
f1 (ppm)

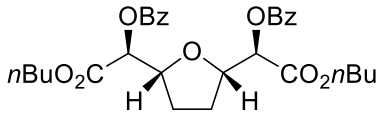

pdornan-2-98Bn-col2.2.fid
172.50
135.26
128.58
128.40
128.23
80.51
73.50
67.34
28.06
f1 (ppm)


OH
OH
PhO
O
OPh
H
H
O
O

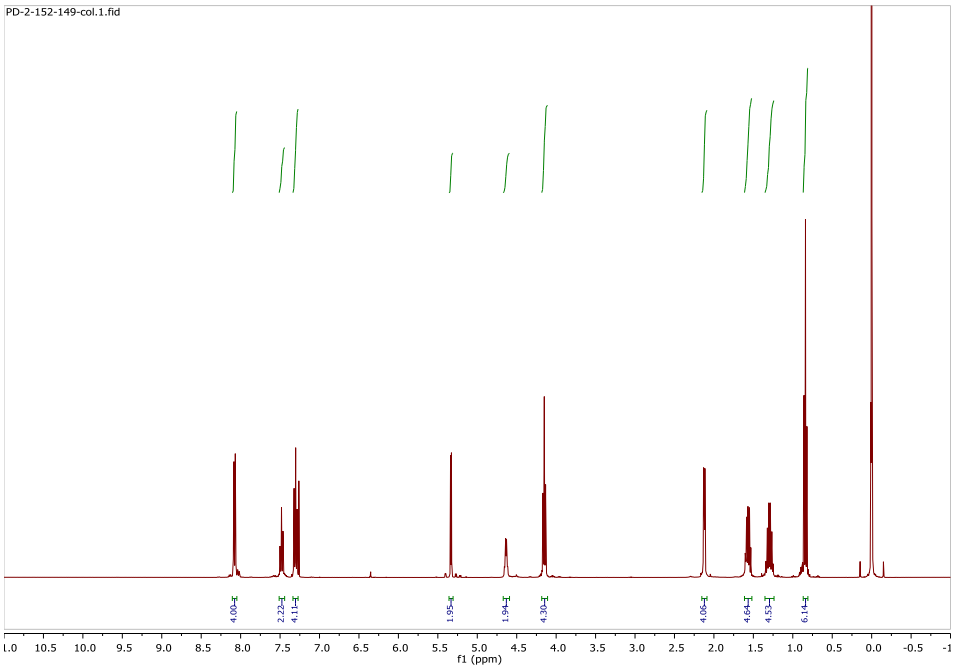
2b

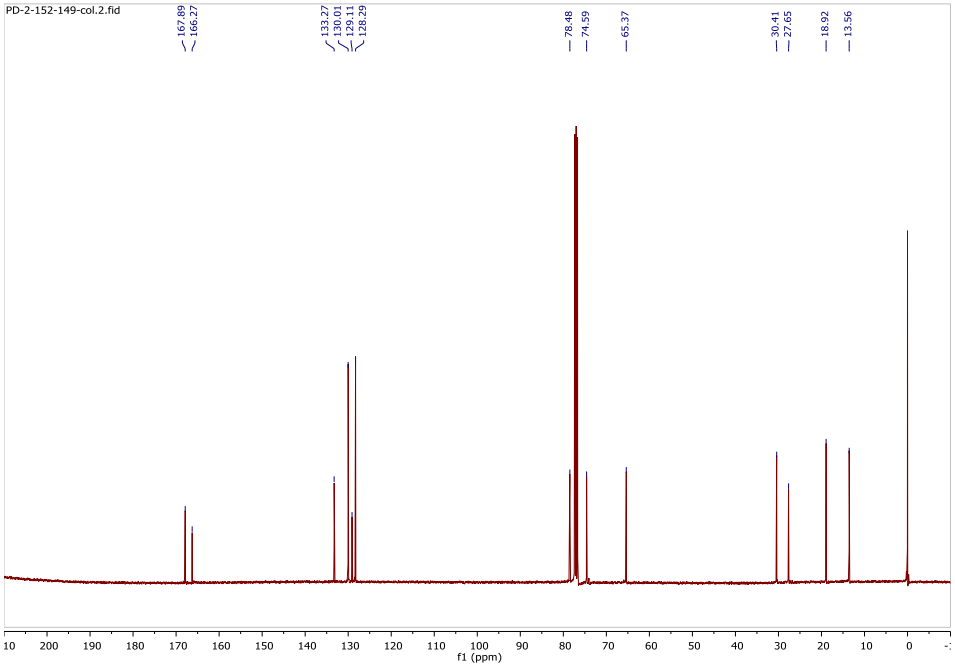

PROTON01
PD-2-106-col2dry
3.99
2.11
4.00
2.01
2.00
1.72
1.96
2.04
f1 (ppm)

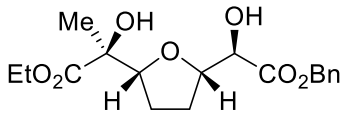

PD-2-106-PA-col2.3.fid
171.48
150.45
129.47
126.13
121.31
80.79
73.56
27.95
f1 (ppm)


OBz
OBz
nBuO2C
O
CO2nBu
H
H

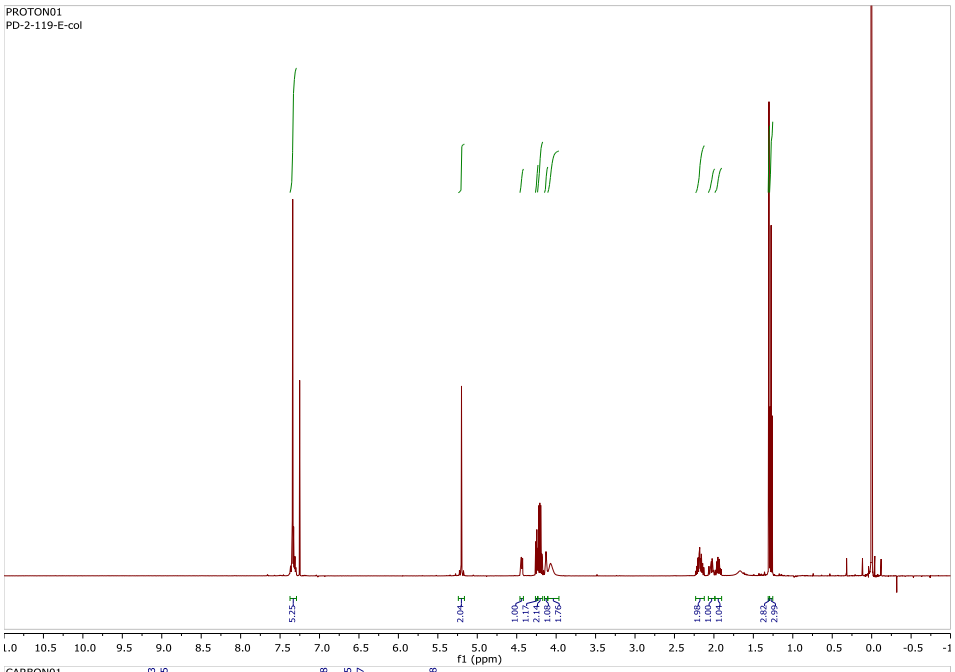
2c

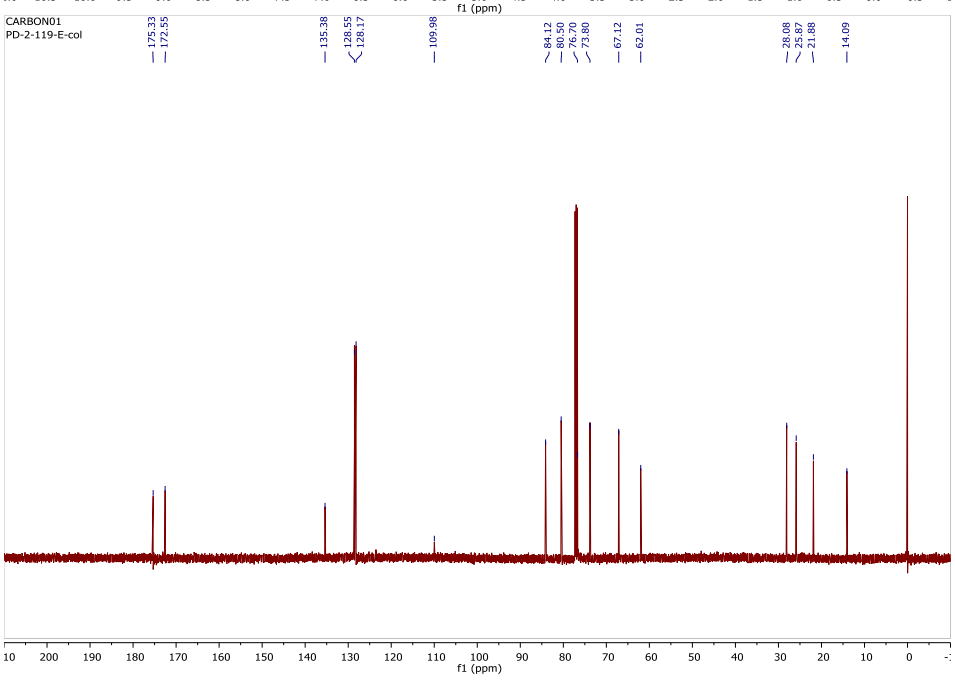

PD-2-152-149-col.1.fid
4.00
2.23
4.11
1.95
1.94
4.30
4.06
4.64
4.53
6.14
f1 (ppm)

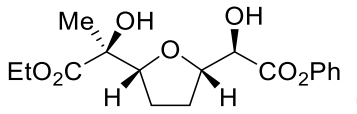

PD-2-152-149-col.2.fid
167.89
166.27
132.27
130.01
129.11
128.29
78.48
74.59
65.37
30.41
27.65
18.92
13.56
f1 (ppm)


Me
OH
OH
O
EtO2C
CO2Bn
H
H

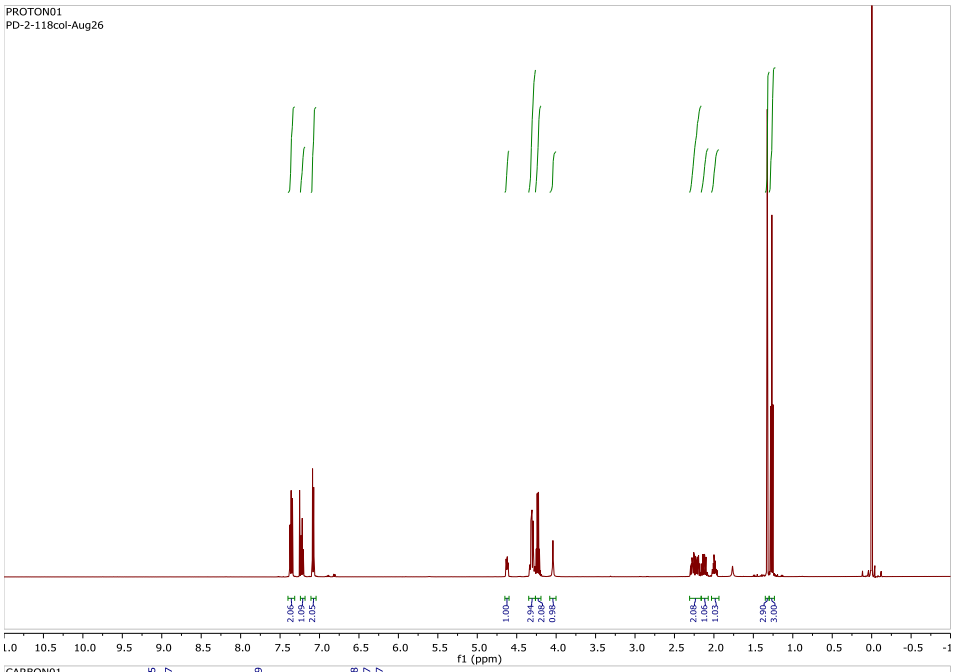
6a

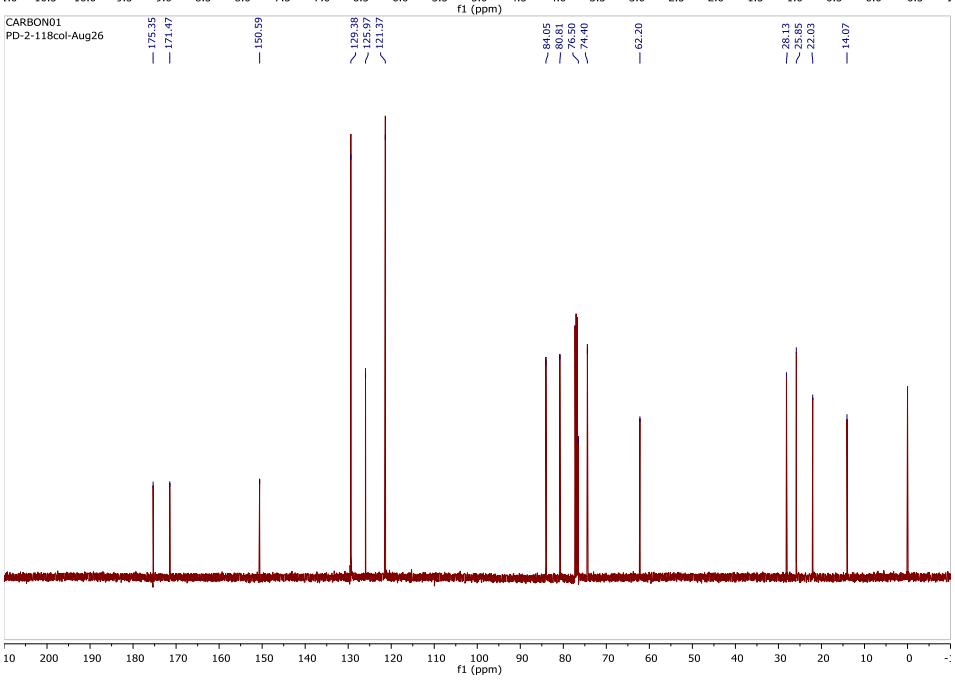

PROTON01
PD-2-119-E-col
f1 (ppm)

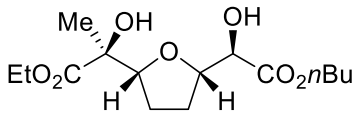

CARBON01
PD-2-119-E-col
175.33
172.55
135.38
128.55
128.17
109.98
84.12
80.50
76.70
73.80
67.12
62.01
28.08
25.87
21.88
14.09
f1 (ppm)


Me
OH
OH
O
EtO2C
CO2Ph
H
H

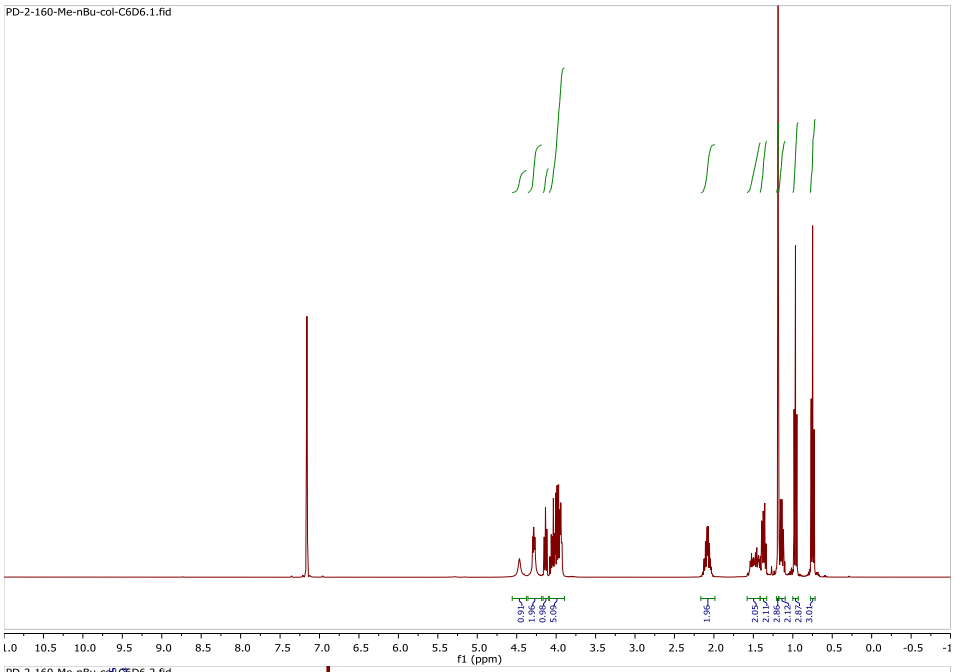
6b

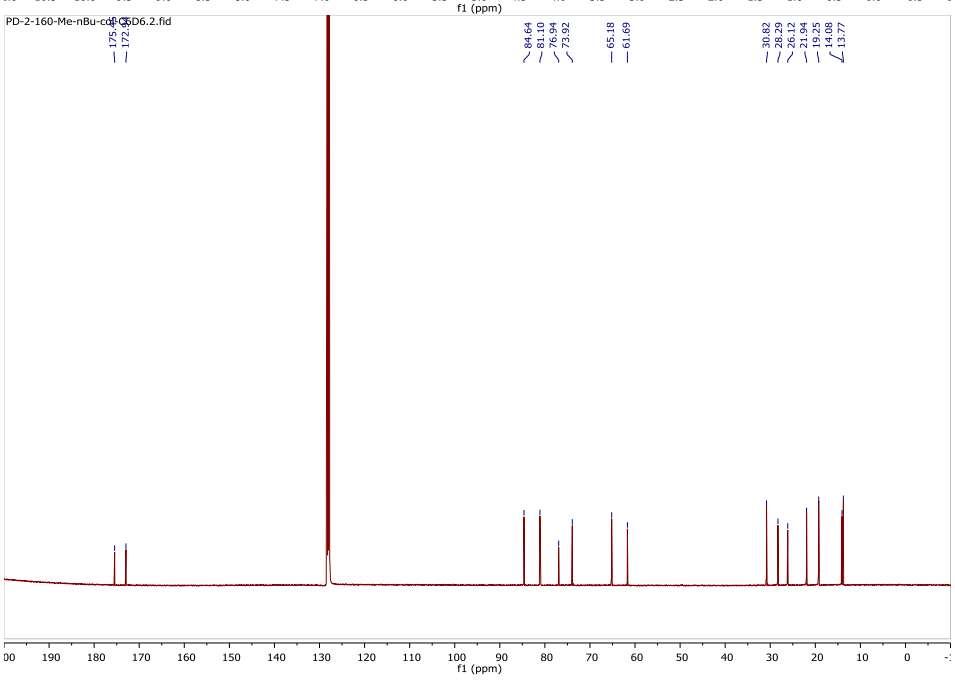

PROTON01
PD-2-118col-Aug26
2.06
1.09
2.05
1.00
2.94
2.08
0.98
2.08
1.06
1.03
2.90
3.00
f1 (ppm)

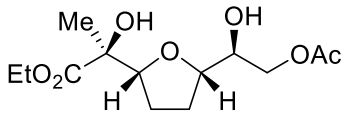

CARBON01
PD-2-118col-Aug26
175.35
171.47
150.59
129.38
125.97
121.37
84.05
80.81
76.50
74.40
62.20
28.13
25.85
22.03
14.07
f1 (ppm)


Me
OH
OH
O
EtO2C
CO2nBu
H
H

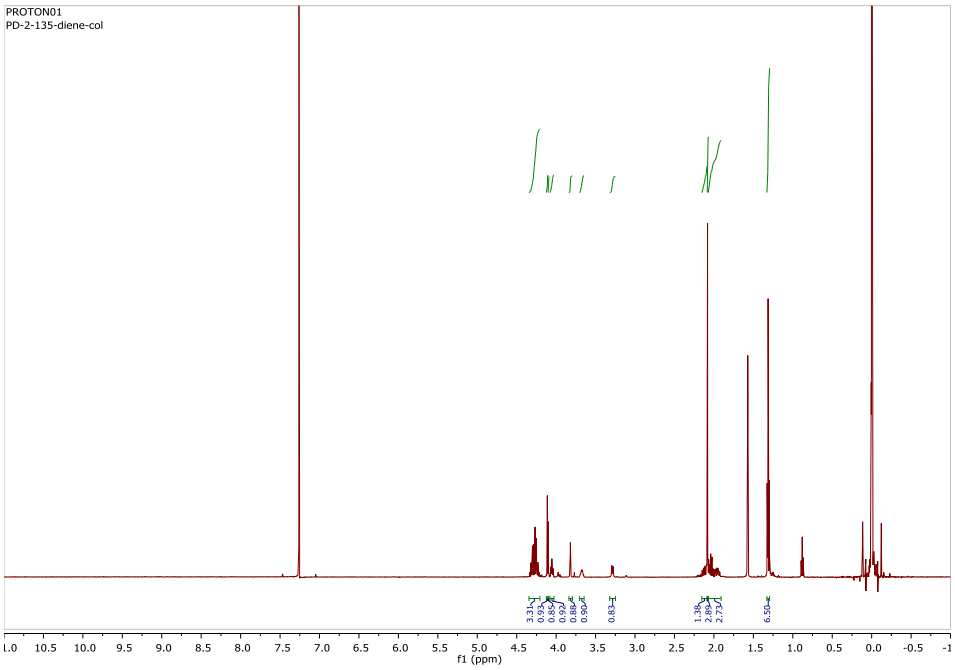
6c

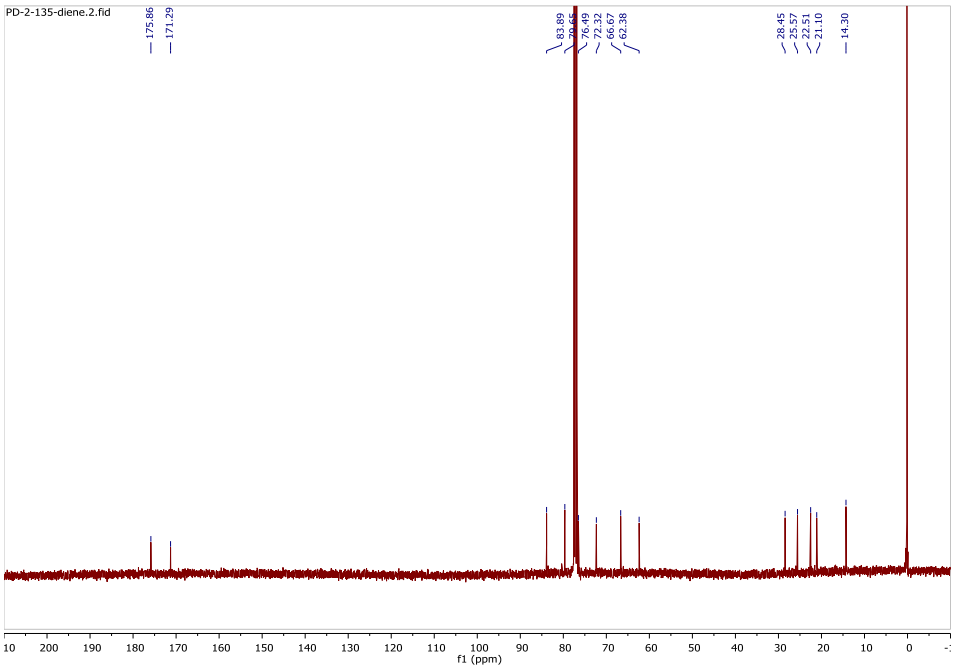

PD-2-160-Me-nBu-col-C6D6.1.fid
0.91
1.96
0.98
5.09
1.96
2.05
2.11
2.86
2.12
2.84
3.01
f1 (ppm)

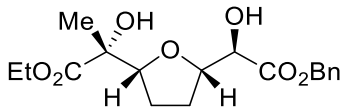

PD-2-160-Me-nBu-col-C6D6.2.fid
175.04
172.49
84.64
81.10
76.94
73.92
65.18
61.69
30.82
28.29
26.12
21.94
19.25
14.08
13.77
f1 (ppm)


Me
OH
OH
O
EtO2C
OAc
H
H

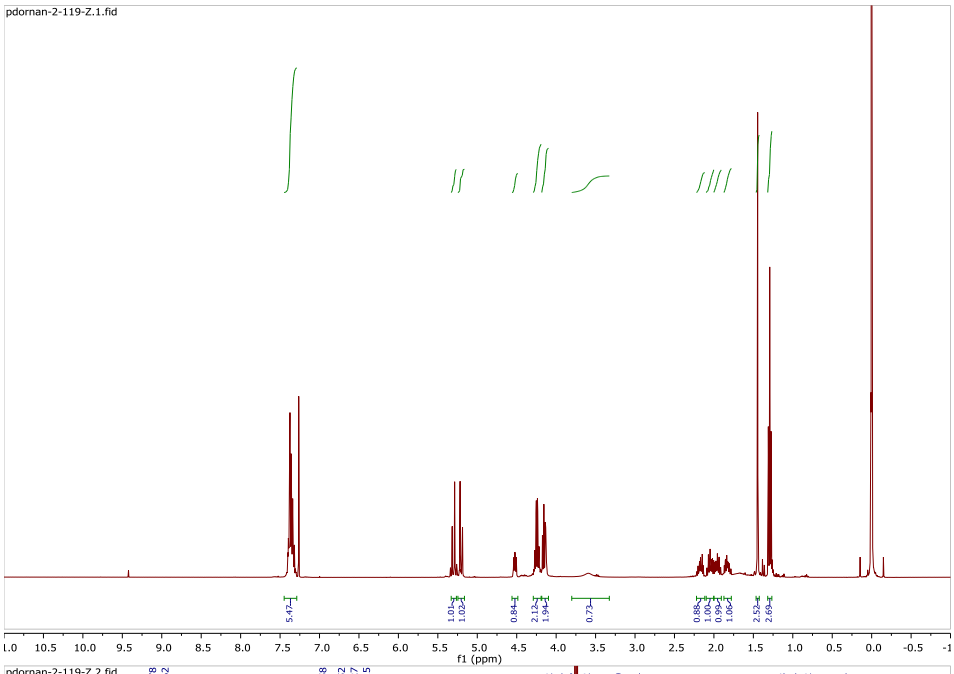
6d

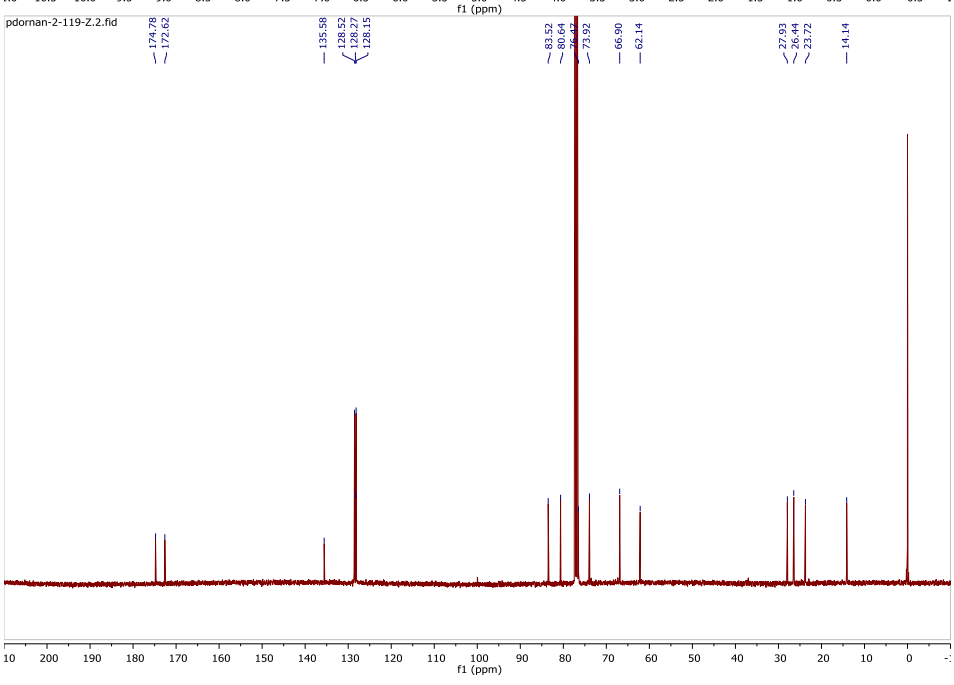

PROTON01
PD-2-135-diene-col
f1 (ppm)

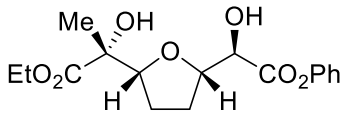

PD-2-135-diene.2.fid
175.86
171.29
83.89
76.49
72.32
66.67
62.38
28.45
25.57
22.51
21.10
14.30
f1 (ppm)


Me
OH
OH
O
EtO2C
CO2Bn
H
H

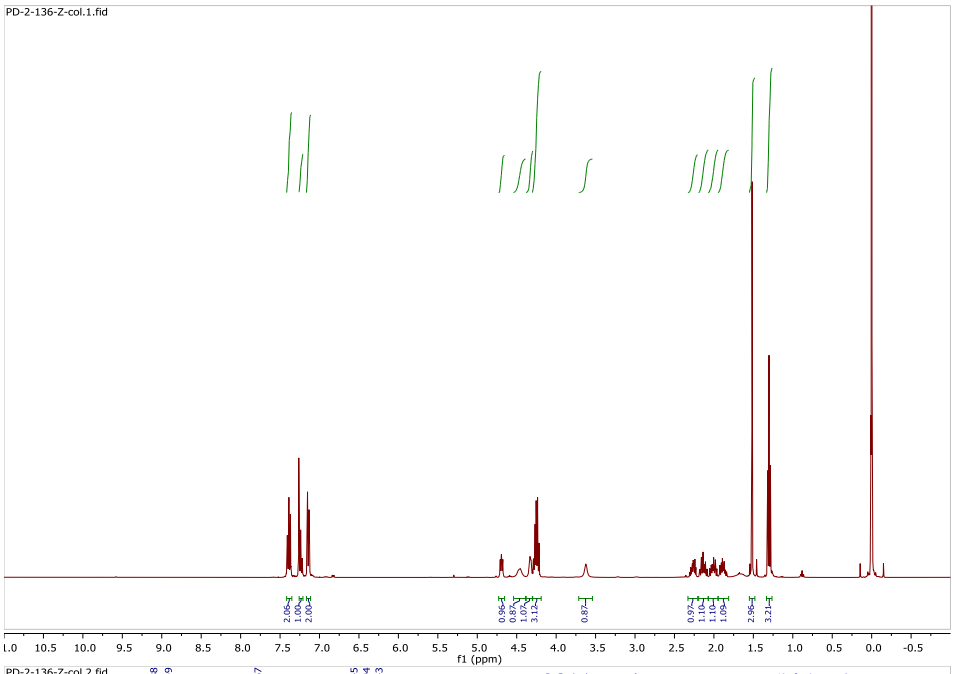
6e

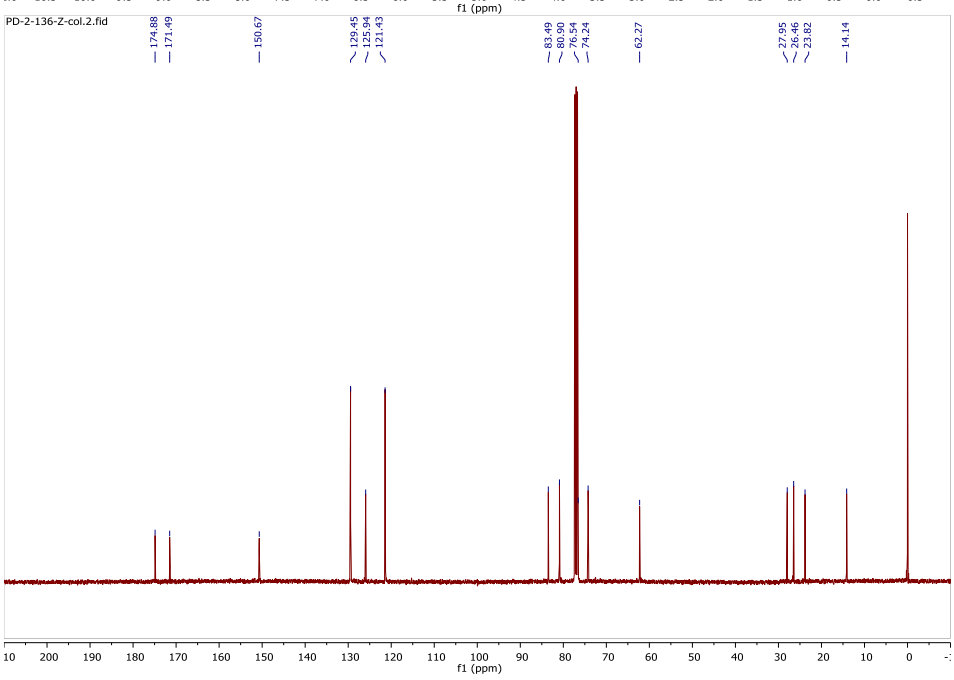

pdornan-2-119-Z.1.fid
f1 (ppm)

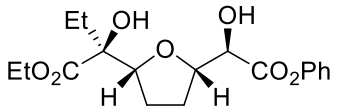

pdornan-2-119-Z.2.fid
174.78
172.62
135.58
128.52
128.27
128.15
83.52
80.64
76.42
73.92
66.90
62.14
27.93
26.44
23.72
14.14
f1 (ppm)


Me
OH
OH
EtO2C
O
CO2Ph
H
H

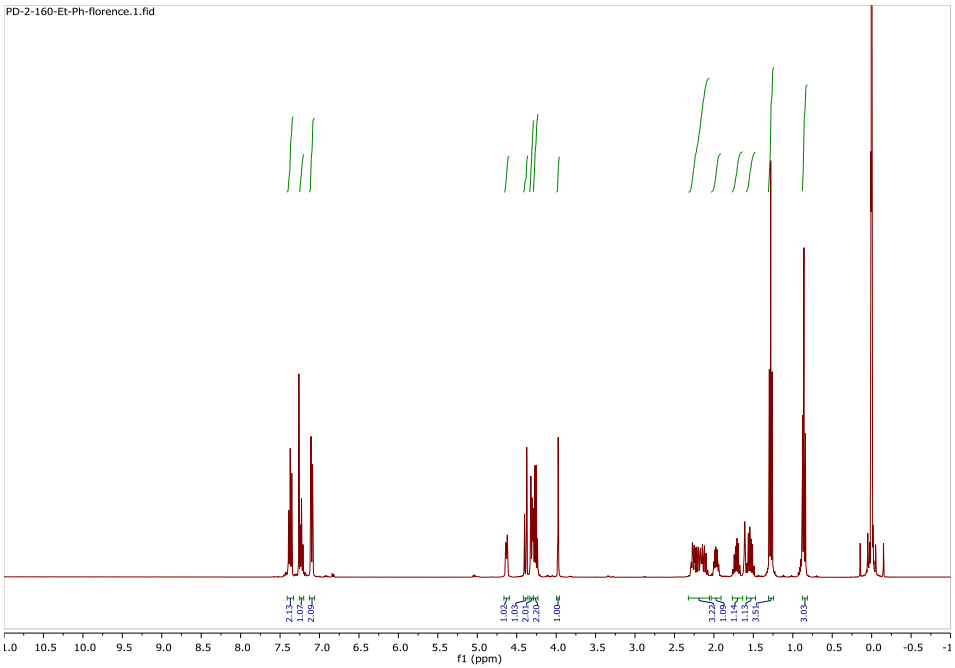
6f

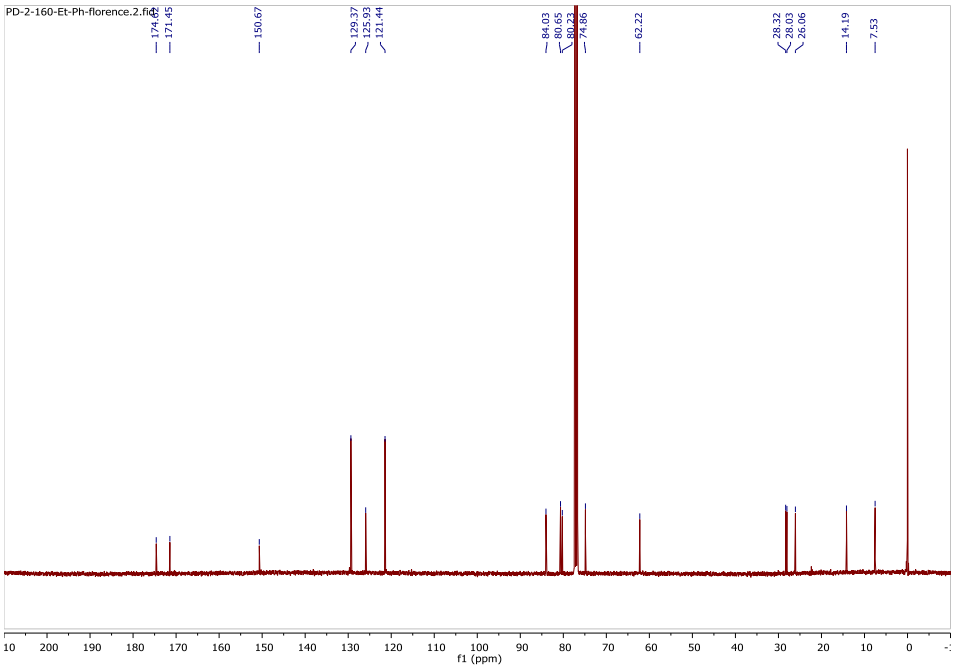

PD-2-136-Z-col.1.fid
f1 (ppm)

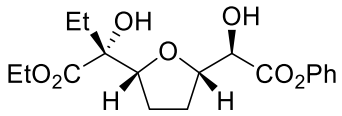

PD-2-136-Z-col.2.fid
174.88
171.49
150.67
129.45
125.94
121.43
83.49
80.90
76.54
74.24
62.27
27.95
26.46
23.82
14.14
f1 (ppm)


Et
OH
OH
EtO2C
O
CO2Ph
H
H

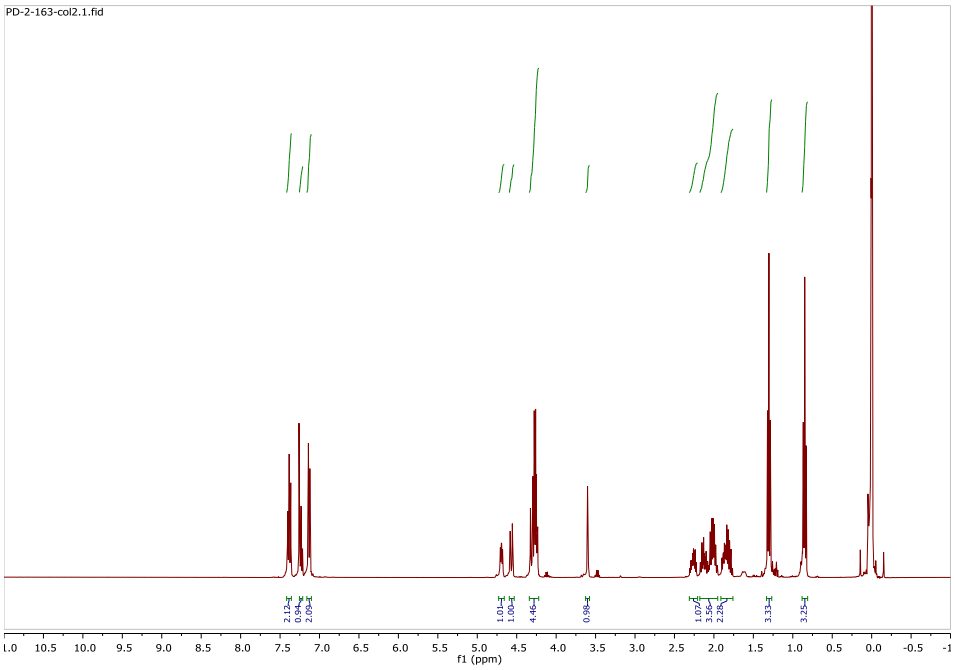
6g

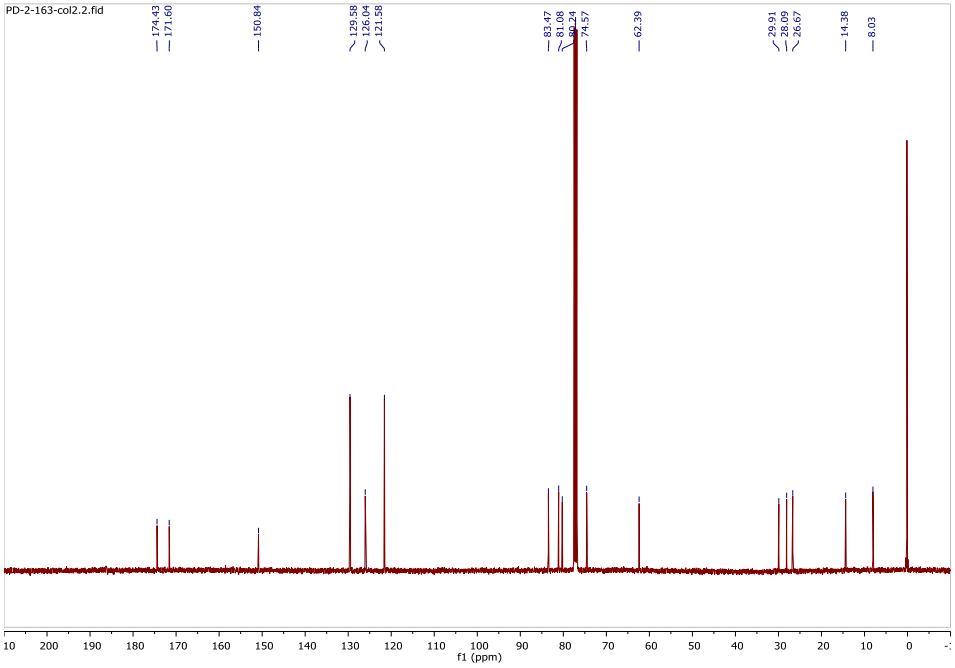

PD-2-160-Et-Ph-florence.1.fid
f1 (ppm)

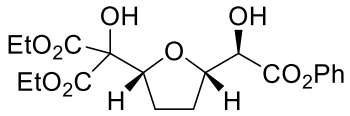

PD-2-160-Et-Ph-florence.2.fid
174.66
171.45
150.67
129.37
125.93
121.44
84.03
80.65
80.23
74.86
62.22
28.32
28.03
26.06
14.19
7.53
f1 (ppm)


Et
OH
OH
EtO2C
O
CO2Ph
H
H

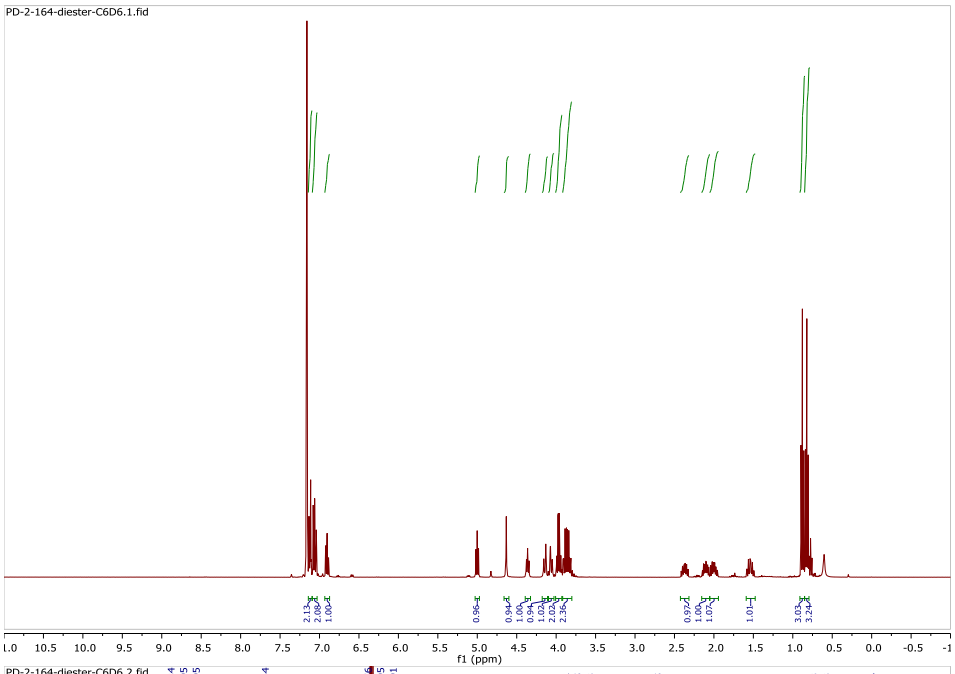
6h

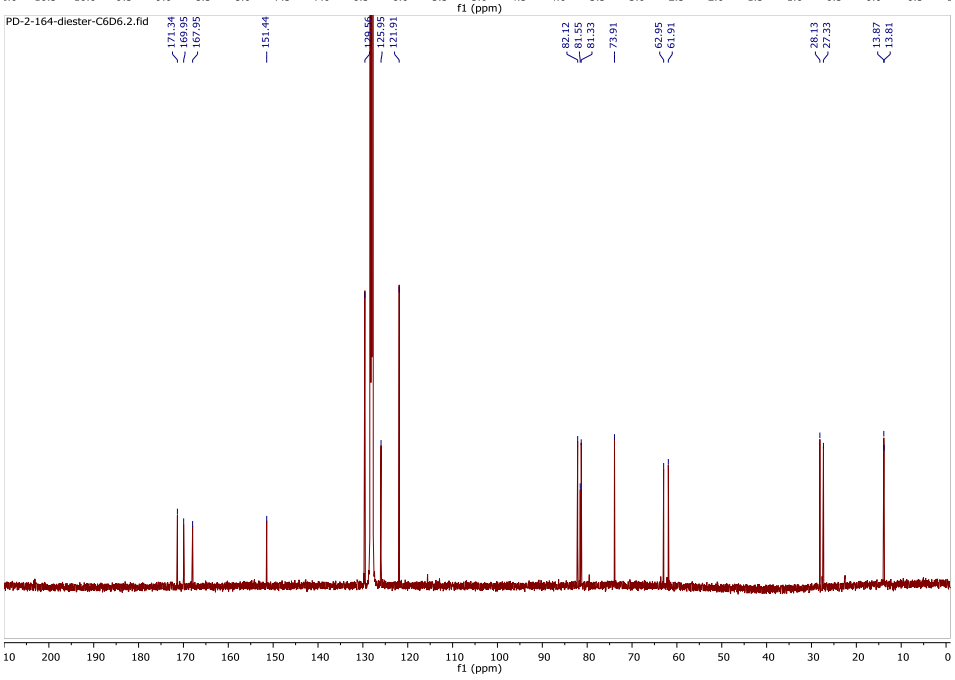

PD-2-163-col2.1.fid
f1 (ppm)

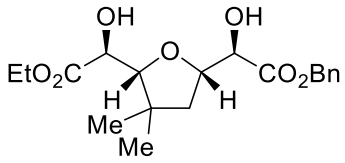

PD-2-163-col2.2.fid
174.43
171.60
150.84
129.58
126.94
121.58
83.47
81.08
80.24
74.57
62.39
29.91
28.09
26.67
14.38
8.03
f1 (ppm)


OH
OH
EtO2C
O
CO2Ph
EtO2C
H
H

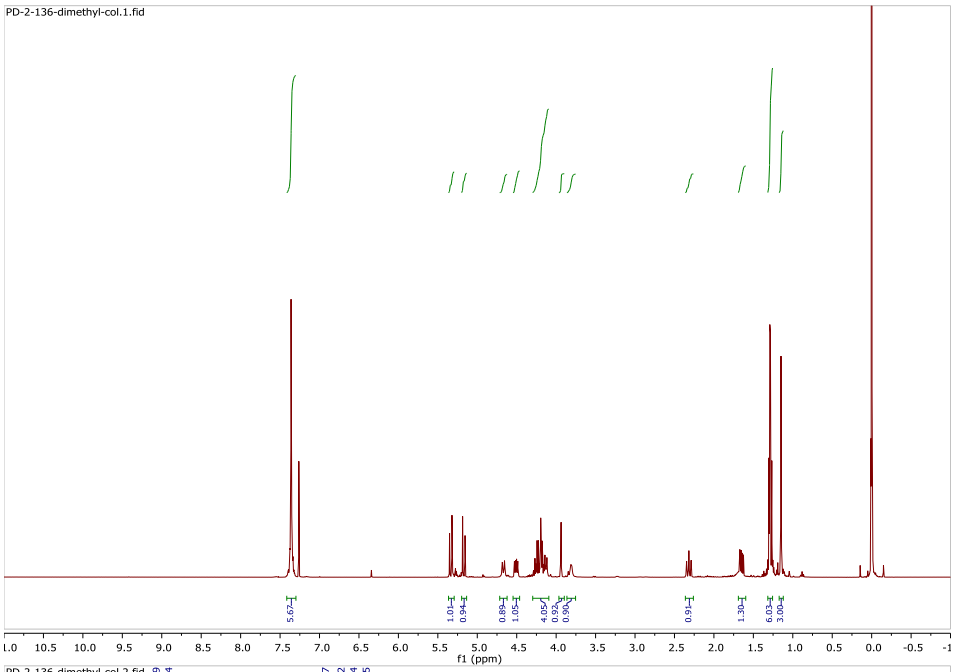
6i

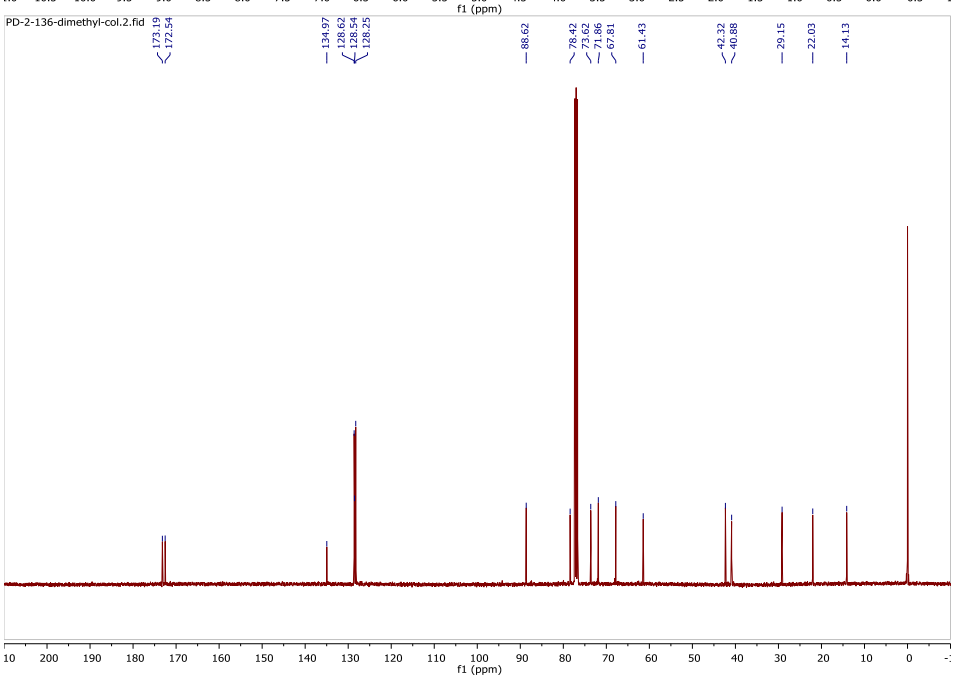

PD-2-164-diester-C6D6.1.fid
f1 (ppm)

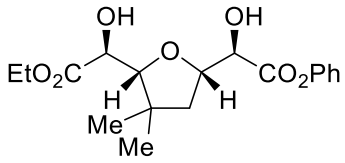

PD-2-164-diester-C6D6.2.fid
171.34
169.95
167.95
151.44
128.56
125.95
121.91
82.12
81.55
81.33
73.91
62.95
61.91
28.13
27.33
13.87
13.81
f1 (ppm)


OH
OH
EtO2C
O
CO2Bn
H
H
Me
Me

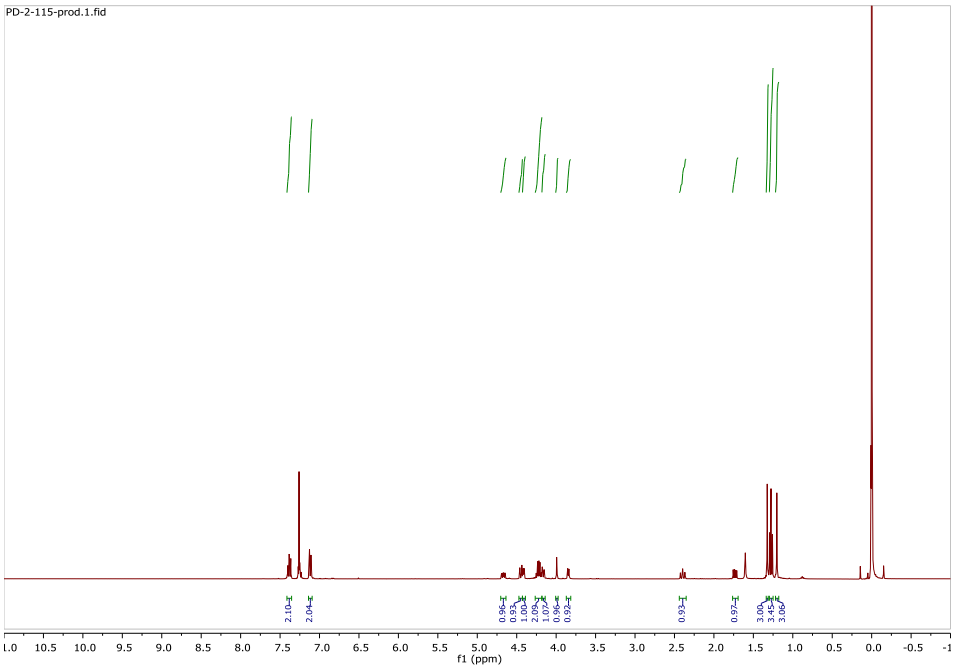
6j

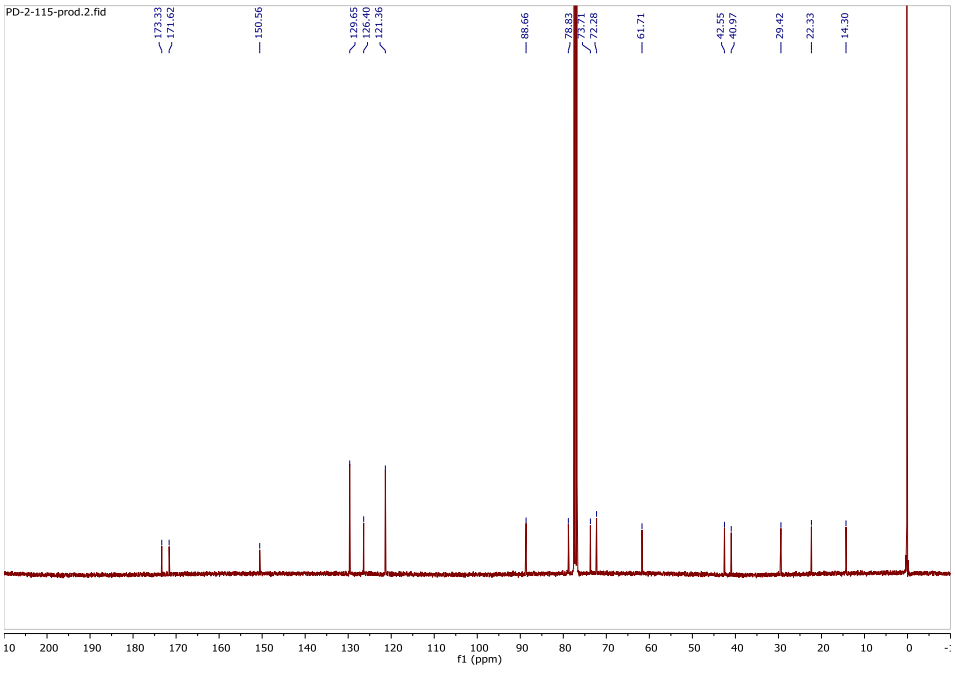

PD-2-136-dimethyl-col.1.fid
5.67
1.01
0.94
0.89
1.05
4.05
0.93
0.90
0.91
1.30
6.03
3.00
f1 (ppm)

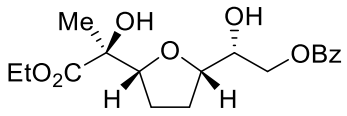

PD-2-136-dimethyl-col.2.fid
173.19
172.54
134.97
128.62
128.54
128.25
88.62
78.42
73.62
71.86
67.81
61.43
42.32
40.88
29.15
22.03
14.13
f1 (ppm)


OH
OH
EtO2C
O
CO2Ph
H
H
Me
Me

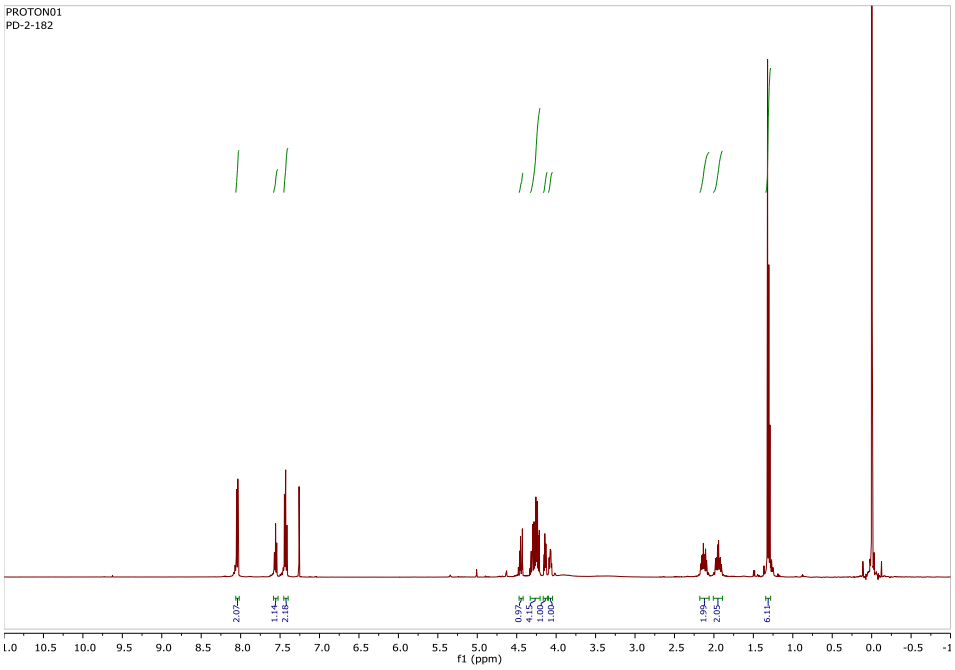
6k

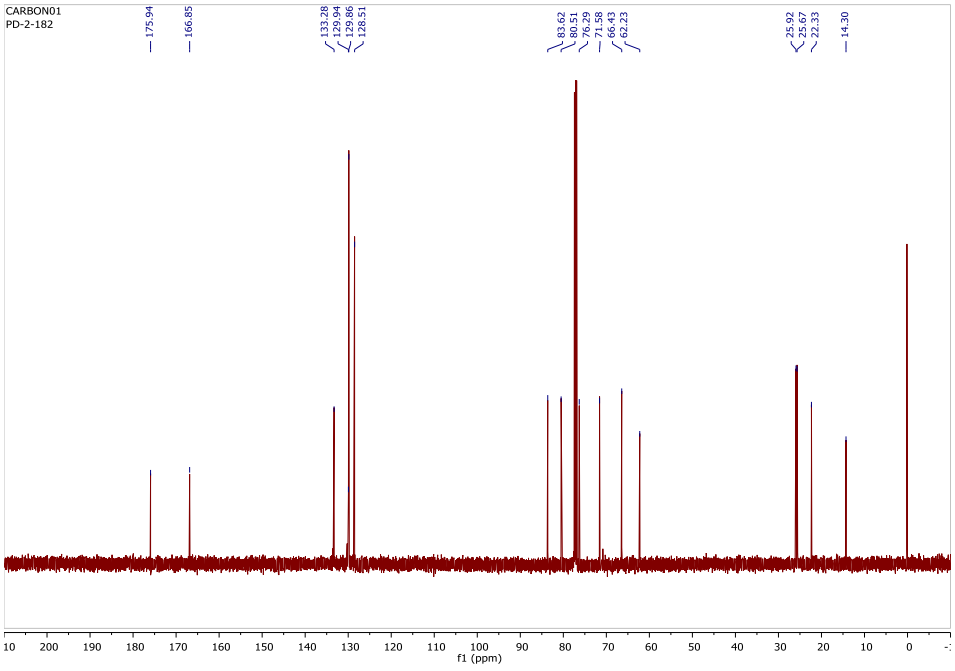

PD-2-115-prod.1.fid
f1 (ppm)

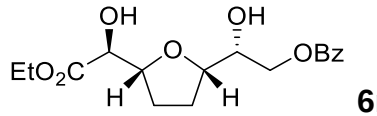

PD-2-115-prod.2.fid
173.33
171.62
150.56
129.65
126.40
121.36
88.66
78.83
73.71
72.28
61.71
42.55
40.97
29.42
22.33
14.30
f1 (ppm)


Me
OH
OH
O
EtO2C
OBz
H
H

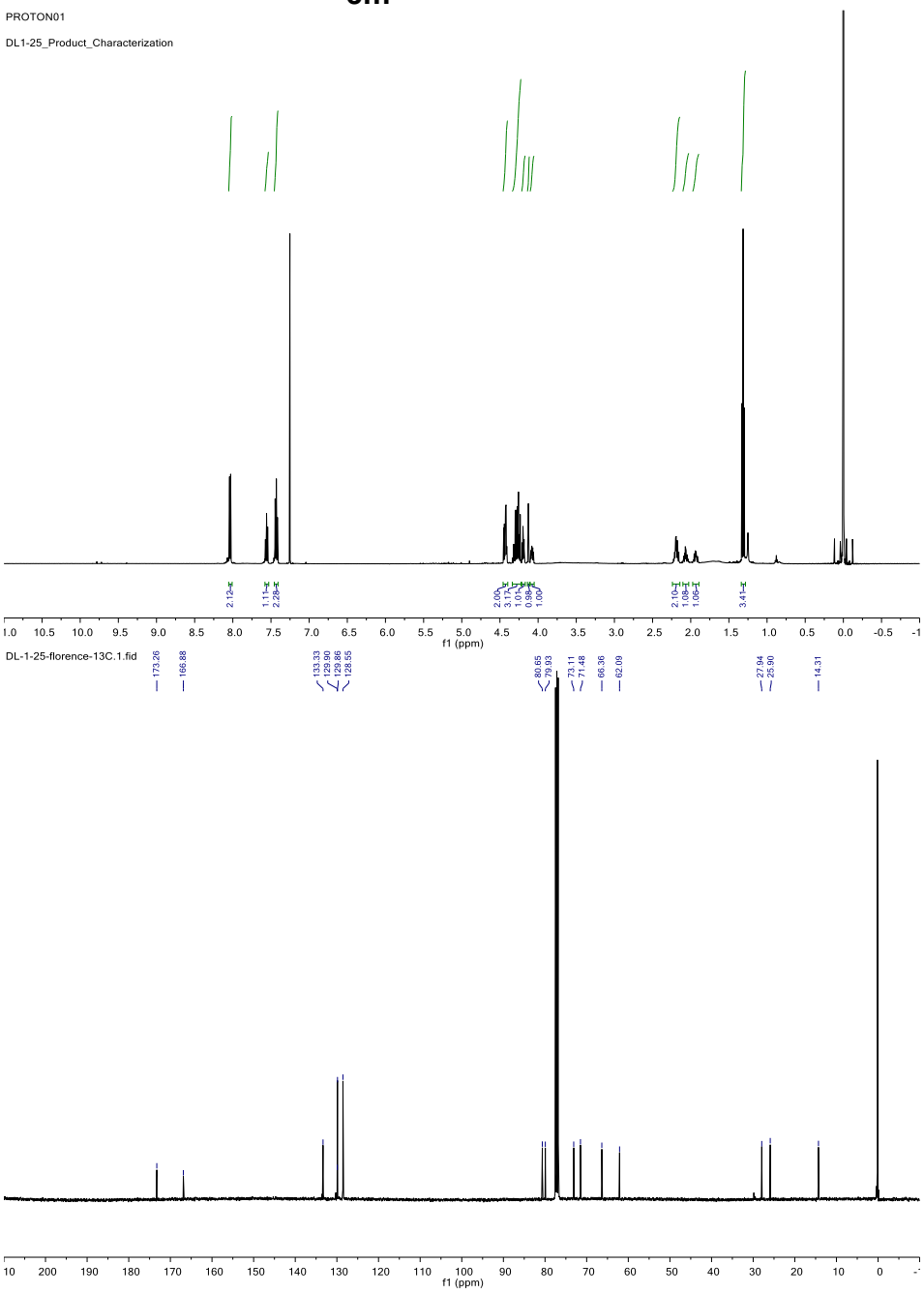
6l

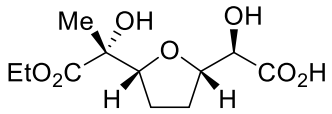

PROTON01
PD-2-182
2.07
1.14
2.18
0.97
4.15
1.00
1.00
1.99
2.05
6.11
f1 (ppm)


CARBON01
PD-2-182
175.94
166.85
133.28
129.94
129.86
128.51
83.62
80.51
76.29
71.58
66.43
62.23
25.92
25.67
22.33
14.30
f1 (ppm)

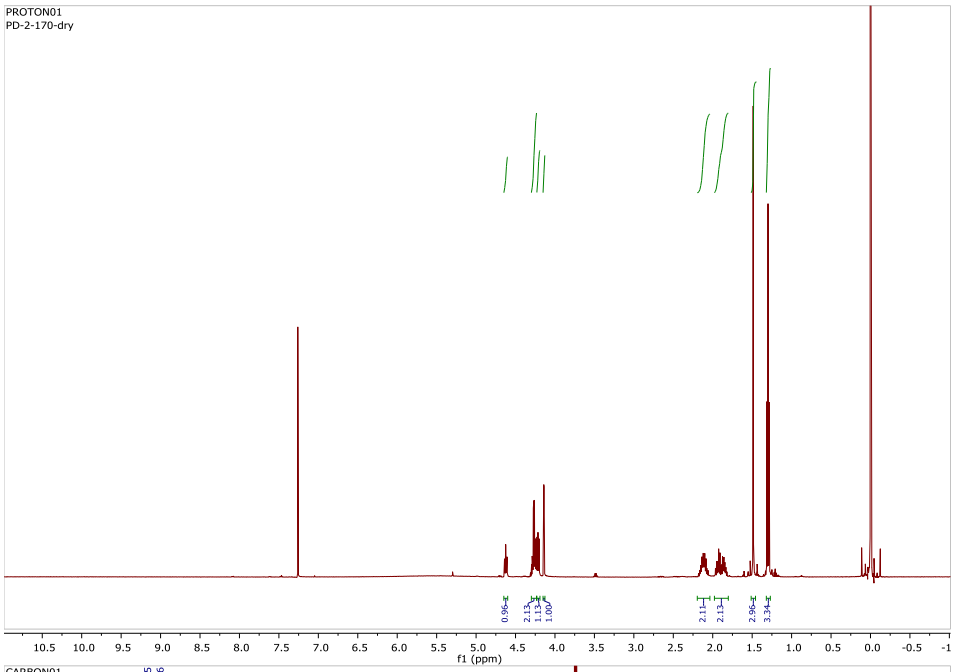

OH
OH
O
OBz
EtO2C
H
H

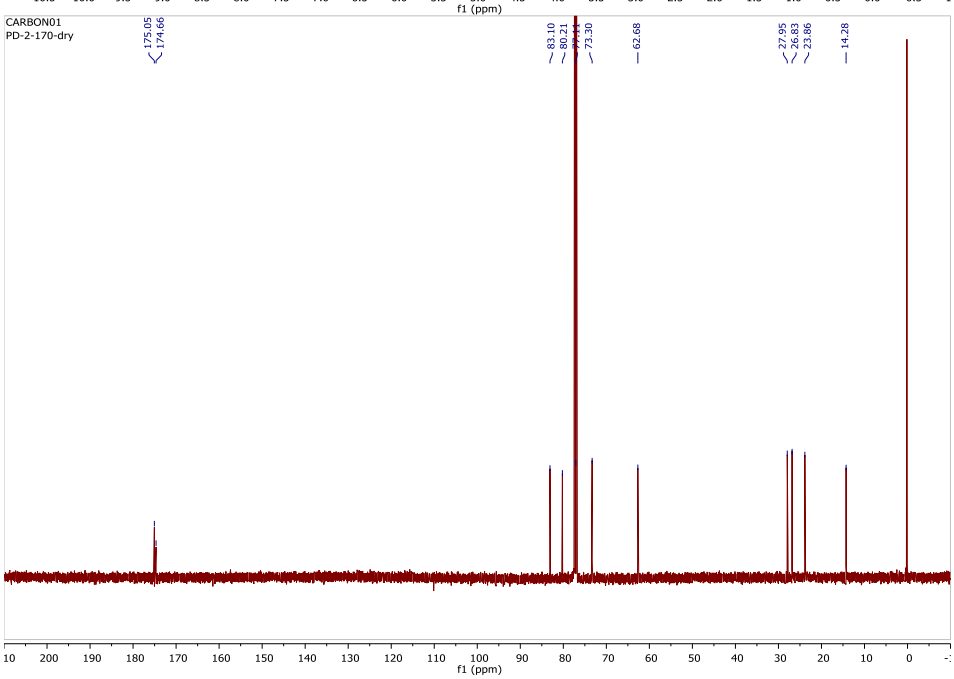
6m


PROTON01
DL1-25_Product_Characterization
2.12
1.11
2.28
2.00
3.17
1.01
0.98
1.00
2.10
1.08
1.05
3.41
f1 (ppm)
DL-1-25-florence-13C.1.fid
173.26
166.88
133.33
129.99
129.86
128.55
80.65
79.93
73.11
71.48
66.36
62.09
27.94
25.90
14.31
f1 (ppm)


Me
OH
OH
EtO2C
O
CO2H
H
H

7a


PROTON01
PD-2-170-dry
0.96
2.13
1.13
1.00
2.11
2.13
2.96
3.34
f1 (ppm)


CARBON01
PD-2-170-dry
175.05
174.66
83.10
80.21
80.00
73.30
62.68
27.95
26.83
23.86
14.28
f1 (ppm)